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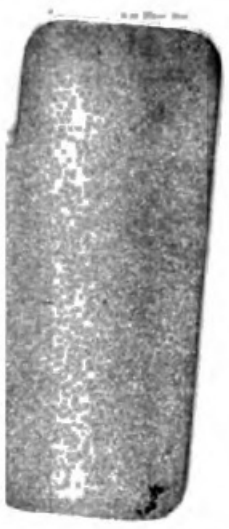

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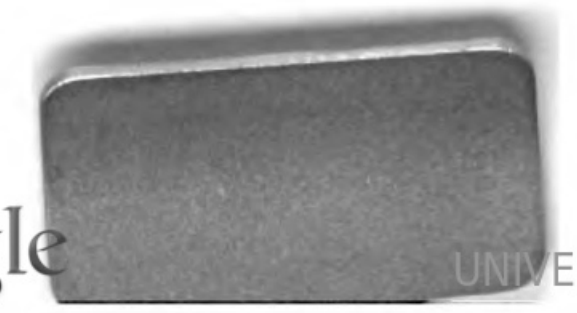

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THE COLLECTED WORKS OF IRVING LANGMUIR

VOLUME 6

STRUCTURE OF MATTER

With a Contribution in Memoriam
by
DR. DAVID HARKER

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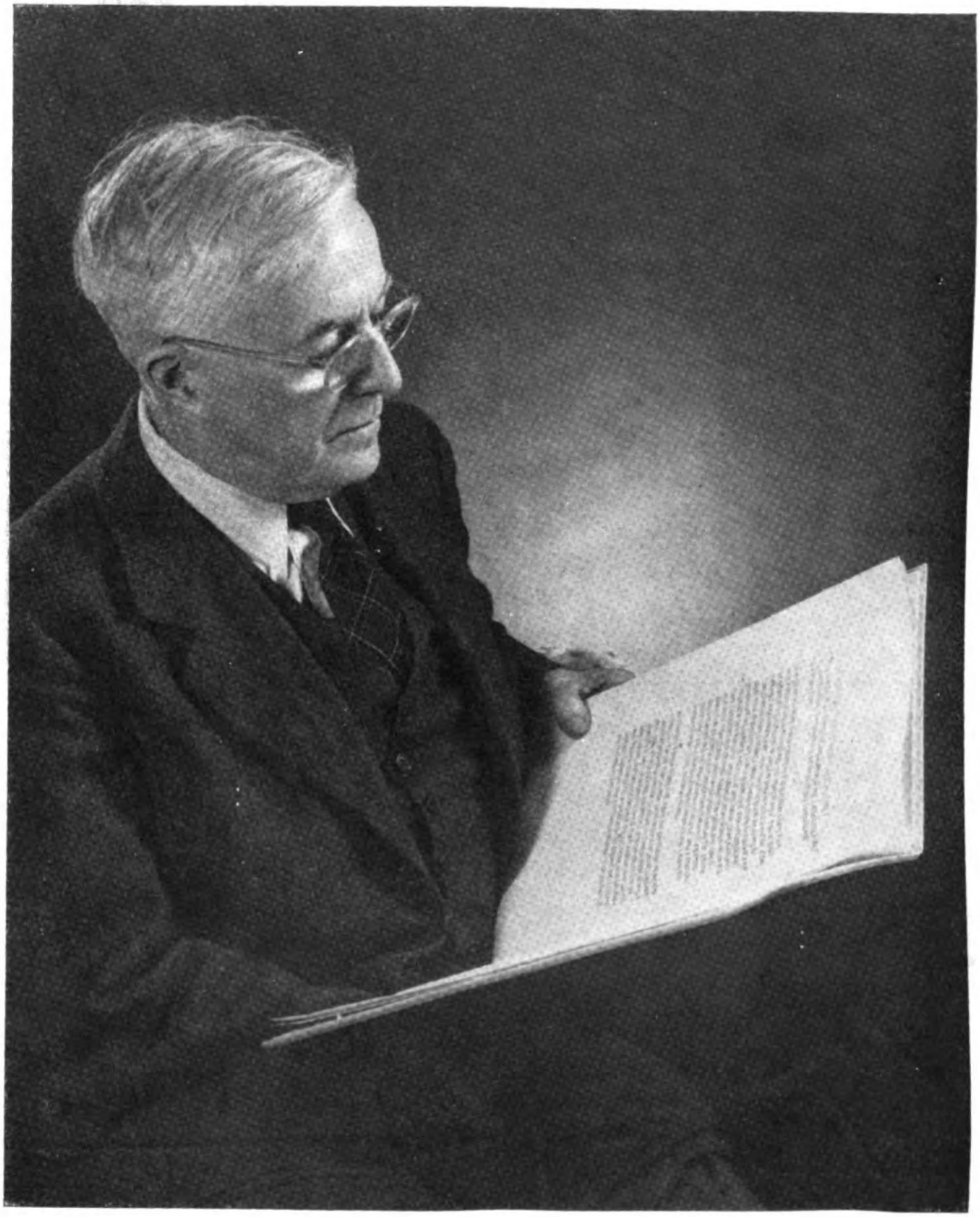

Irving Langmuir — Research Scientist
General Electric Research Laboratory — 1909–1957
Nobel Prize Winner–1932

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THE COLLECTED WORKS OF
IRVING LANGMUIR

WITH CONTRIBUTIONS IN MEMORIAM
INCLUDING
A COMPLETE BIBLIOGRAPHY OF HIS WORKS

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Volume 6

STRUCTURE OF MATTER

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FOREWORD

THE PLAN to publish a memorial to Irving Langmuir, including all of the scientific output of his brilliant career in research, was announced to me by Captain I. R. Maxwell, managing director of Pergamon Press, late in 1958. My associates and I were asked to aid the venture by providing editorial advice and counsel, by enlisting the cooperation of scientific friends and acquaintances, and by assisting in the collection and identification of material. Our enthusiasm for the project and our willingness to cooperate sprang from two important considerations.

First, Langmuir's career provides an outstanding example of how free, but discriminating, inquiry in pure science may yield not only vital new knowledge and understanding of nature, but also a great bounty of practical usefulness for society. Secondly, Langmuir's associates hold him not only in great respect, but in very great affection as well. Hence the preparation of these volumes has been more than a service; it has been a labor of love.

The original plan was to publish Langmuir's works in three or four volumes, but for very good reasons, which developed during the course of the project, the series has grown to twelve volumes. The quantity of Langmuir's published scientific work proved to be far greater than we had estimated, and some previously unpublished wartime research and reports on meteorological studies were of such importance that their inclusion in the volumes was mandatory. Moreover, some exceptionally interesting philosophical papers and publications served to round out the literary portrait of Langmuir as a man and as a scientist.

My associate editors, Sir Eric Rideal and Professor P. W. Bridgman, have contributed generously from their great wealth of knowledge and their intimate acquaintance with Dr. Langmuir. It is a pleasant duty to acknowledge that the many members of the Honorary Editorial Advisory Board have participated in this venture with enthusiasm, and that their editorial contributions to the separate volumes have added tremendously to the appraisal and interpretation of Langmuir's collected works. I particularly want to acknowledge with gratitude the valuable work of Professor Harold E. Way of Union College who, in the capacity of Executive Editor, has carried the major task of assuring that our responsibilities and commitments were fulfilled.

I first met Irving Langmuir in the General Electric Research Laboratory when I joined the research staff in 1930, but our first meeting might equally well have taken place on a ski hill in the Adirondacks, at Lake George where

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he liked to spend the summer, or on a climb on Mt. Marcy, for he had a prevailing love of the out-of-doors. Whether in the Laboratory or in the mountains, an intense curiosity about natural phenomena constantly pervaded his thoughts. In fact, I have never met anyone else who was *so well coupled to nature*.

I am sure that, like all observant people, Langmuir perceived the beauty of nature as portrayed by the qualities of form, color, mass, movement, and perspective. In addition, however, Langmuir was delighted and entranced even more by the challenge to understand the working of nature as portrayed in the phenomena of everyday life — clouds, ripples on water, bubbles in ice, the temperature fluctuations of air and of water, the plastic quality of snow, the flight of a deer fly, and the thousands of "simple" phenomena which nearly everyone takes for granted. These manifestations of nature held endless fascination for Langmuir, and he constantly challenged himself to explain basic phenomena in terms of known laws of science. Of course, the same curiosity characterized his work in the Laboratory, and hence, provided the unifying motivation for his career, whether at "work" or at "play".

Langmuir's scientific work is so completely and perceptively described and appraised in the separate volumes of this work that only a few general comments and observations are appropriate, or indeed possible, at this point.

One striking feature of his research method was its instrumental simplicity. Although his career extended into the glamour age of science, characterized by large, impressive, and expensive machinery such as the cyclotron, the synchrotron, and particle and radiation diffraction equipment, his own experiments were almost invariably simple and uncluttered. He seemed positively attracted to simple experimental techniques, in refreshing contrast to what sometimes appears to be a fashionable reliance on impressive and expensive complexity of research equipment. His work with heat transfer in gases, and later with electron emission phenomena from metals, employed laboratory glassware of stark simplicity. His studies of surface films, especially films on water, employed beautifully simple experimental equipment. The Laboratory work on aerosols and smokes, and later on the nucleation of supercooled clouds, was all carried on with apparatus that could be assembled from the equipment of a typical home. His classical experiments on the "speed of deer fly" came about as close as possible to the string, wax, and paperclip approach to science; yet they sufficed to establish the essential facts sought by the investigation. Probably few scientists, before or since Langmuir, have gained so much important new knowledge of nature with such simple research equipment.

Similarly, Langmuir preferred to work with a few collaborators, rather than a large group or team of researchers, for this favoured a close contact with the work on a participating basis. His ability to apply mathematical analysis to physical problems was of a high order, and he divided his time about equally between experimental work and theoretical work. The combination

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of outstanding experimental and analytical ability which he possessed occurs but rarely in a single individual; most scientists have somewhat greater interests, aptitudes, and hence accomplishment in one area or the other.

Langmuir almost invariably worked on an intense basis and was generally completely preoccupied with his current problems. His concentration was exceptional, and he might pass you in the hall without seeing you. If you reminded him of it, he would smile and acknowledge that he was highly excited about some experiments that were in progress, or about some calculation that was presenting some puzzling aspects.

We spend a good deal of time and thought nowadays on the question of motivation for scientists, seeking to understand the source and character of their drive. In Langmuir's case, one needs to inquire no further than his curiosity. This pronounced trait provided an intense internal source of motivation, which constantly drove him to inquire and probe and test hypotheses until a pattern of understanding was developed. When he was on the trali of an exciting mystery, which was usually the case, his intense concentration was remarkable to behold.

Langmuir's career contributes much to our understanding of creative output in research. For example, on the perennial question of creativity and age, it has been held by some that the bulk of human creative work is accomplished in early adult life, say in the age bracket between 25 and 35 years. It is probable that some purely statistical information might support this view. However, I would disagree strongly with the corollary conclusion that creative ability is characteristic of this age bracket. In the Laboratory, it is not unusual for creative young workers to acquire a greater span of research guidance, counselling, and even management responsibility as their career matures, and hence their creative contribution will, to a corresponding degree, appear in the work of others. I believe that in such cases scientists are generally not less, but more creative with advancing age, frequently up to and even through retirement. It is clear that purely statistical information would not readily reveal this fact.

It is interesting to examine Langmuir's career as an example of a scientist who remained in active research up to and through retirement, to see what role age played in his output. In Volume 12 we have depicted Langmuir's achievements as a function of his age, using his scientific *publications* as evidence of his gross scientific output, and his *principal accomplishments* as evidence of his creative output. The resultant charts show remarkably constant productivity throughout his scientific career, and even through retirement. Throughout this period Langmuir published an average of five to six scientific papers per year. His principal accomplishments, both scientific and practical, took place almost uniformly over the period of his researches. Certainly no "creative age" can be identified in his career. The example of Langmuir's scientific history does not prove the general thesis, but from the observation

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of many research careers, I am persuaded that human creativity in science is not a significant function of age.

Creative output, however, *is* a function of many other factors that comprise the research environment. One important factor is the changing field of research. Some of the most creative scientists in the history of the General Electric Research Laboratory have worked intensively in one field for a period of some years, and have then changed quite abruptly to a new field as a source of fresh stimulation and new challenge. It is evident that in a period of 5 years, or so, one can bring a fresh point of view to a new field, make a major contribution, and perhaps exhaust one's ideas on the subject. At that point of fruition, there is a great temptation to sit back and bask in a reputation for eminence which has been established in a specialized field of science. The more courageous scientist, however, will be challenged, or will, like Langmuir, challenge himself to enter a new field. This requires courage, because in the new field he will be a neophyte but, at the same time, a scientific entrepreneur with a reputation at risk, and this risk may not pay off.

Langmuir's career exemplifies the courageous entrepreneur in science. It would be difficult to find a common denominator, except curiosity, in many of the fields of science in which he made basic contributions. He never hesitated to attack new fields, such as protein monolayers, the generation of smoke, or meteorology, which were completely new and, hence, challenging territory to him. In each of these diverse fields, and in a great many others, he has made major basic contributions.

Some discussion of the very important applied aspects of Langmuir's scientific work is appropriate. It is a fact that, although his prevailing motivation in research was curiosity about all natural phenomena, he was always perceptive of the practical usefulness of research results, and he himself suggested possible practical applications of many of the new phenomena which he discovered. He was generally able to communicate his enthusiasm to applied scientists and engineers interested in the proposed application and to give them guidance in its exploration.

It is interesting to speculate on the way that Langmuir's career might have developed had he chosen an academic, rather than an industrial environment for his work in science. My personal belief is that his research would, in any environment, have resulted in a high order of scientific accomplishment. Although he evidenced little interest in teaching, he was in fact an outstanding teacher, and in a university he would have exerted a great influence on students who might have been fortunate enough to be in contact with him. But I doubt if an academic career for Langmuir would have, or could have, developed the great bounty of useful results for society which did come from his exposure to a creative industrial scientific environment. The human and economic impact of gas-filled lamps, high-vacuum electron tubes, atomic-hydrogen welding, space charge emission phenomena, techniques and discoveries in

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surface chemistry, thyratron arcs (with A. W. Hull), and cloud seeding techniques has been very great indeed, and in most of these developments the influence of his research environment has been unmistakable.

Wherever Langmuir worked, or might have worked, the world is vastly better because of him, and both his former associates and colleagues, and the public at large, bear a tremendous debt of gratitude for his genius in science and for his perception of human need.

June 15, 1960

C. Guy Suits
Vice-President and Director of Research
General Electric Company
Schenectady, New York

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PREFACE TO VOLUME 6

MUCH of Irving Langmuir's work in the first five volumes could well be classed as physics. It might be pointed out, however, that during the time he was working in the field of thermionics and gaseous discharge, he was also doing a great deal of research on the structure of atoms with emphasis on valence. As early as 1919 he published a paper extending the Lewis theory of atomic and molecular structure. This more general paper was followed by others applying his theories to specific atoms such as helium. He sought a better explanation of the spectra, the ionization potential, the optical properties, and the magnetic properties of the helium atom than that provided by the Bohr theory. While much of his work has been modified by Heisenberg, Pauli, and others, the basic framework he helped to develop has not greatly changed.

It was natural that Langmuir should use crystal structure to check his theories on molecular structure, and the latter papers in Part 2 of this volume are devoted to his work in this area.

When Langmuir became interested in an area of research, such as the structure of matter, he concentrated on it as indicated by the fact that over half of the papers in this volume were published in the two-year period, 1920, 1921.

Dr. David Harker, head of the Biophysics Department of the Roswell Park Memorial Institute in Buffalo, New York, and a man with an outstanding background of work on structure of matter, was invited to write the contributed article for this volume.

HAROLD E. WAY
Executive Editor

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INTRODUCTION TO VOLUME 6

A CONTRIBUTION IN MEMORIAM

BY DR. DAVID HARKER

IN THESE days it is a little hard for structural chemists, like the present writer, to recall the strange disorder in the science of chemistry that preceded the development of the electronic theories of valence. A large part of organic chemistry could be thought about in a beautiful, logical way by using the concepts for what we would now call covalent bond theory, but most of inorganic chemistry could not be brought into any kind of order by this way of thinking. There were two chemistries: organic, that was fun because predictions could be made with some assurance, and inorganic that was fun, because the result of a new experiment was very often a complete surprise.

A brilliant idea, which we can now see to have been the first step toward unifying the two chemistries, seems to have occurred almost simultaneously to G. N. Lewis and Irving Langmuir: the electron pair bond between atoms and the stable electron octet on the outer surface of the atom. Lewis published the first description of the idea[1] and, with its aid, gave a very satisfactory explanation of the chemical behavior of all of the light elements and such of the heavy ones as have atomic numbers near those of the noble gases. Lewis implied that the electrons in atoms were in fixed positions and seems to have thought of them as at the corners of cubes, or as pairs at the vertices of tetrahedra, symmetrically enclosing the atoms. To account for the behavior of hydrogen and helium he postulated that the first shell of electrons could hold no more than two electrons.

Lewis' paper thus presented a picture of each atom as consisting of a small nucleus with a definite number of unit positive charges, around which electrons, each carrying a unit negative charge, were arranged in shells, of which the first consisted of two electrons across the nucleus from one another, while the remaining shells were cubical (or tetrahedral) arrangements of eight electrons, each succeeding shell larger than the preceding one and surrounding it. Chemical behavior was presented as caused by a strong tendency for electrons to form pairs and octets. Pairs could be shared between atoms to complete octets in their outer shells, or electrons could be added to or subtracted from an atom until its outer shell became a complete octet (or a pair,

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in the case of the first shell). Some examples will show how this picture of atomic structure agrees with the facts of chemistry:

The atomic structure of neon, with atomic number 10, would consist of a nucleus carrying 10 positive unit charges surrounded by two shells of electrons, the inner one of two electrons and the outer one of eight. This is a stable structure, according to Lewis' postulates, in agreement with the chemical fact that neon never combines with other atoms to form compounds.

Fluorine, with atomic number 9 — one less than neon — has atoms with an outer shell of 7 electrons. Thus, fluorine would have a strong tendency to acquire an electron from its surroundings to complete an outer octet, and thus become a negatively charged fluoride ion ($F + e^- \rightarrow F^-$), or to share an electron with another atom in order to accomplish the same purpose. The element fluorine is thus composed of molecules consisting of two fluorine atoms bound together by a shared electron pair which completes the octet of the outer shell of each. This shared electron pair was considered to correspond to the valence bond of organic chemistry.

Sodium, with atomic number 11, has one more electron than neon, and this must occupy one of the cube corners of the third shell. By donating this electron to its environment a sodium atom could achieve the neon-like electron configuration and become a positive ion ($Na \rightarrow Na^+ + e^-$). The formation of sodium fluoride from the elements sodium and fluorine could be thought of as the transfer of an electron from each sodium atom to each fluorine atom to produce pairs of ions, Na^+ and F^-, arranged so as to minimize the electrostatic potential energy, i.e. a hard solid, such as sodium fluoride actually is.

Many other examples could be given of the correspondence between Lewis' theory of atomic and molecular structure and the objective facts of chemistry. There are, however, several respects in which this theory is not completely satisfactory. In the first place, the electrons were considered to be stationary, but no forces were included in the theory to keep them so. Secondly, the limitation to pairs and octets of electrons left the chemistry of what we now call the "transition elements" unexplained. Lewis did indeed include all the noble gas structures in his catalogue of stable electronic configurations — even though the atoms of krypton, xenon, and radon (then called "niton") could not be composed of a shell of two electrons and several shells of eight electrons — but did not find a reasonable way to use these structures in explaining the chemical properties of the transition elements.

Irving Langmuir seems to have been engrossed with the problem of chemical binding at about the time that G. N. Lewis' paper appeared, and quite probably had been thinking along the same general lines. On March 3, 1919, he submitted a paper[2] which modifies and extends the Lewis theory of atomic and molecular structure to such an extent that it comes close to unifying the whole of chemistry under one theoretical framework. Furthermore,

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the way in which Langmuir treats the arrangement of the electrons in atoms seems to foreshadow the concepts of quantum mechanics.

The space around one atomic nucleus is divided into cells of equal volume and each cell can contain one or two electrons, except the two cells nearest the nucleus which can contain only one electron each. No specific location is given the electron in its cell. (This smacks of the cells in position-momentum space occupied by electrons in statistical quantum mechanics, even to the possibility of two electrons — now with opposed spins — which can occupy a single cell.) These cells were arranged in concentric layers about the atomic nucleus, with their average radii in the ratios 1:2:3:4: — and their thicknesses about equal, so that the volumes of the successive layers — or shells — are in the ratios $1^2:2^2:3^2:4^2$: —. The first shell is postulated to contain two cells, therefore the succeeding layers must contain, respectively, 8, 18, 32, — cells. The number of cells in the shells is always even and this is made the basis for postulating a two-fold symmetry in the distribution of the cells; Langmuir chose the symmetry element to be a reflection plane of symmetry passing through the atomic nucleus. The cells in all shells are distributed so as to preserve this symmetry, and, in addition, each shell is given an additional symmetry of its own: the second shell has four cells above and four below the equatorial mirror plane shaped like octants of a sphere, the third shell has nine cells on either side of the equator one of which encloses the pole of the equatorial plane with the other eight equally spaced around the circumference of the shell between the pole and the equator, etc.

The structure of each (isolated) atom consists of an electron distribution about the nucleus, according to which the shells are filled in order: first the innermost shell with one electron per cell, then the second shell with one electron per cell, then by placing another electron in each cell of the second shell, then the third shell with one electron per cell, then with two, etc.

According to this picture, the noble gases consist of atoms with structures consisting of shells completely filled with electrons, except that the innermost shell contains only one electron per cell and the outermost shell may contain either one or two electrons in every cell. The structures of these atoms would be given, according to Langmuir, by the following table:

Atom	Atomic No.	Electrons in shell				Outermost shell, electrons per cell
		I	II	III	IV	
He	2	2				1
Ne	10	2	8			1
Ar	18	2	16			2
Kr	36	2	16	18		1
Xe	54	2	16	36		2
Rn	86	2	16	36	32	1

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These are postulated to be the most stable structures, in agreement with the chemical facts. Their high symmetry was used to justify this agreement.

It is interesting to compare these ideas with those now accepted. We now speak of orbitals — electron distributions which may contain two, one, or no electrons — these are almost the same as Langmuir's cells. Modern orbitals are not spatial boxes, but are diffuse affairs which, at least in theory, fill all space. However, each atomic nucleus is surrounded by orbitals — whether empty, or containing one or two electrons each — and the average distance from the nucleus of each orbital essentially determines the order in which the orbitals are filled as electrons are added to the atom. When we remember that quantum theory had just been when Langmuir made his postulates, that neither quantum mechanics with its indeterminacy principle, nor the Pauli exclusion principle had yet been formulated, we can only marvel at the intelligent insight and practical grasp which pervades his concepts of atomic structure.

In formulating the kinds of chemical binding, Langmuir and Lewis used essentially identical postulates: the stability of the electron pair, and the tendency of atoms to complete noble gas structures, even by sharing electron pairs if necessary. For the atomic numbers up to that of scandium (21), and for the heavier elements whose atomic numbers differ from those of noble gases by not more than three units, i.e., the elements rubidium, cesium, (francium), strontium, barium, radium, yttrium, lanthanum, actinium, bromine, iodine, (astatine), selenium, tellurium, (polonium), arsenic, antimony, and bismuth (elements whose chemical properties have become known only after Langmuir's and Lewis' papers had appeared, are in parentheses) the Langmuir and Lewis theories give almost exactly the same results. There are many elements, however, with atomic numbers so far from those of the nearest noble gases, that the simple ideas just mentioned cannot reasonably be expected to apply; these are the elements not included in the foregoing list, and which are mostly now included under the term "transition elements."

Langmuir made a historically important attempt to rationalize the chemical behavior of the transition elements. He reasoned that the removed of four or more electrons from an atom would require more energy than could normally be expected to be furnished by the completion of octets on neighboring atoms (although such powerful octet formers as oxygen and fluorine occasionally accomplished such feats, for example in SF_6, OsO_4, MnO_4^-) and that the attachment of fourfor more electrons to an atom would create such a concentration of negative charge that not even the stabilization provided by the formation of a noble gas structure could keep it from blowing apart. He therefore constructed what Linus Pauling would now call a stochastic theory, based partly on a quantitative feeling for ionization potentials, partly on a postulated symmetry of the electron distribution in the 18 and 32 cell outer shells of these atoms, and partly on arguments derived from the chemical

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properties of the substances in question. (He also used some arguments based on some postulated magnetic properties of electrons in atoms which added but little to the consistency of his theory and have almost no historical significance.)

Having explained that such elements as titanium, vanadium, etc., up to iron, cobalt and nickel usually have electropositive valences of two, three, or four, because higher valences require the supplying of too much energy, Langmuir then shows how nickel can achieve such electronic symmetry in its outer shell that its structure has some of the stability which is so strongly pronounced in the noble gases. The ten outer electrons of nickel are arranged five above and five below the equatorial plane. In each hemisphere one electron occupies the cell surrounding the pole, while the other four occupy alternate ones of the eight remaining cells. This structure is not stable enough to prevent a nickel atom from losing two electrons to become Ni^{++} with a structure like that of a neutral iron atom, but is stable enough to make cuprous ion exist, with the same electronic structure and to prevent zinc and gallium from forming any other ions but Zn^{++} and Ga^{+++}. Cupric ion, Cu^{++}, is an anomaly here, since its structure is like that of neutral cobalt, and its quite frequent and stable existence would lead one to expect the probable existence of trivalent zinc, which does not exist. (Modern theories can do no better, however.) The chemistry of the elements germanium, arsenic, selenium and bromine is considered to be dominated by their proximity to the noble gas krypton. Langmuir's atomic theory is applied in much the same way to the remaining transition elements, and to the rare earths, but it must be admitted that the theory grows less simple and convincing as the heavier elements are reached. Langmuir, like many modern chemists, expected uranium to resemble neodymium. "However, the properties of uranium do not bear out this supposition. Uranium is not closely related in its properties to neodymium, nor in fact does it closely resemble any other element. It would seem therefore that it is not safe from our present knowledge to make definite predictions as to the properties of other possible elements of this period."[3]

All in all, Langmuir's theory of the electronic structure of atoms and of the part this plays in their chemical properties is a significant advance over the Lewis theory, and is much nearer to what theoretical chemists use today than was anything previous to Langmuir's and Lewis' work. They have brought both the valence of the organic chemist and the valence of the inorganic chemist into the framework of a single theory, which is essentially the same as is used today, and Langmuir had made a start toward explaining the still not well understood chemistry of the transition elements.

Even the most modern points of view have failed to rationalize the properties of some substances. The great stabilities and low boiling and melting points of nitrogen, carbon monoxide, and nitric oxide still do not fit well into any theory of molecular structure. Langmuir assumes that the surfaces of the

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molecules of each of these substances consists of a shell of eight electrons similar to that of a noble gas, and that the inner part of these molecules consists of two nuclei, each with its inner shell of two electrons, and another pair — or, in the case of nitric oxide, triplet — of electrons associated closely with the intervening space between the two kernels. This picture is certainly at least as satisfactory as anything yet postulated, although the correct way of looking at these structures is obviously still unknown. Langmuir notes that the paramagnetic susceptibility of nitric oxide is probably associated in some way with its having an odd number of electrons, but does not mention that oxygen molecules, which have an even number of electrons, are also paramagnetic. How could he violate his principle of the predominant stability of electron pairs? We now are forced to assume two unpaired electrons in the oxygen molecule, on the basis of spectroscopic evidence which had not been interpreted in 1919. No theory which would have predicted this phenomenon from first principles has yet been worked through, although our confidence in modern quantum mechanics is such that we believe a complete calculation would lead us to predict two unpaired electrons in the oxygen molecule.

Langmuir spent much thought on the question of whether or not the electrons in atoms and molecules were in motion. He found the idea of static electrons distasteful, and tried in many ingenious ways to devise electronic motions which would be consistent with the general pattern of his and Lewis' theories of atomic structure, yet would provide a reasonable force preventing the electrons from falling into the nucleus of an atom. In his papers on "The Structure of the Helium Atom"[4] he shows that the assumption of coplanar orbits for two electrons circulating around the helium nucleus in the same direction, as postulated by Bohr, lead to an incorrect ionization energy for helium. He then assumes a model in which the two electrons in a helium atom travel in opposite directions toward a collision on one side of the nucleus, then bounce back toward another collision on the opposite side, then both swing forward again, etc. This model (most remarkably) gave about the correct ionization energy for helium. More important, it showed that states of motion for electrons, other than those contemplated by the Bohr theory of atomic structure, could give better agreement with experiment.

With the modern equipment provided us by Heisenberg's Indeterminacy Principle, Pauli's Exclusion Principle, the Heitler-London-Slater-Pauling theory of the chemical bond, Pauling's hybrid electron orbitals and theory of resonating electron states, etc., it is easy to guess at an electronic structure for a molecule which will usually — but not by any means always — agree with the experimental facts. All this equipment was developed in the 1920's and 1930's, after Langmuir's and Lewis' classic work. It is truly gratifying to us who knew and admired these great chemists that the general framework of the theory of atomic and molecular structure they worked out has really not changed in essentials. We use the electron pair (two electrons with

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opposed "spins"), the completed shells of eight and eighteen electrons, the sharing of electron pairs to connect atoms by "covalent bonds", and the formation of completed shells (octets and noble gas structures are some of them) to make positive and negative ions which then attract one another by electrostatic forces, i.e., "electrovalence".

If nothing more had been accomplished by the Langmuir-Lewis theory of atomic structure than the unification of the two chemistries — organic and inorganic — by the introduction of a scheme into which both the "bond" of the organic chemist and the "valence" of the inorganic chemist would fit, this theory would have a great place in scientific history. As it has turned out, the Langmuir extensions of the original joint theory seem to have been exactly in a direction toward later developments in the ways of *thinking* about chemical combination.

And this important and complicated subject is covered by only one of the chapters of the many in these volumes commemorating the work of Irving Langmuir!

Molecules and Crystalline Structure

The existence of a complicated situation in some realm of natural phenomena was always a challenge to Irving Langmuir, and he was one who accepted such challenges. He could not allow a complexity to exist; he immediately set about finding a simple, natural way of correlating the phenomena. His command of the weapons of the scientific arsenal was immense and his endurance and ingenuity in their use was spectacular. These traits of Langmuir's are apparent in his treatment of the situation in chemistry which provided two different kinds of chemical combination, depending on whether the substances under study were organic or inorganic. The results of his attack on the complexities of valence theory and atomic structure were given previously. The victory, while not complete, was so compelling that the theoretical structure of the subject of chemistry was completely changed. The new structure of chemistry is still abuilding, but its builders have never needed to tear out any important part of the foundation laid by Langmuir and Lewis.

As soon as Langmuir had found a simplifying idea and had used it to destroy the complex situation which caused its birth, he set out to apply it to new situations. Sometimes these new situations had previously looked simple, and it occasionally happened that Langmuir's characteristically energetic attack appeared to some other scientists to be creating more complexity than it removed. Usually this was only an appearance — the subject was almost always better off after the Langmuir treatment than before it; but it was never quite the same again.

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An example of such a subject is crystallography. Previous to 1912 it had been the province of a gentle, pure minded, academic fraternity developing a neat and logically beautiful array of theories and a set of delightfully crisp and clear cut experimental results. The theories of crystal symmetry and structure of those days could mostly be checked only against the angular relationships between the faces on real crystals, and the effects of crystalline material on visible light. In 1912 this charming, secluded scientific refuge was invaded by a powerful army of physicists, led by Max von Laue, and W. H. and W. L. Bragg, who began to discover experimentally the actual distribution of atoms and molecules within crystals, using the property of crystals that they diffract X-rays. A. W. Hull, a member of the staff of the General Electric Research Laboratory, soon became interested in this line of research and may have directed Langmuir's thoughts toward the structures of crystals. In any event, Langmuir seized on crystal structure as a powerful way of checking his theories of molecular structure.

In a paper closely following the one on "The Arrangement of Electrons in Atoms and Molecules" which was previously discussed, Langmuir uses the data of crystallography to support his ideas of chemical structure; this second paper is entitled "Isomorphism, Isosterism and Covalence."[5] This paper seems to me to have been the foundation of what is now called "crystal chemistry", and which is one of the new subjects introduced into crystallography since 1912 that has brought it into a prominent position in physical science — and destroyed its almost monastic calm.

Langmuir, basing his reasoning on the theories of chemical structure outlined in the previous chapter, predicted that the electronic structures of nitrogen, carbon monoxide, and cyanide ion should be the same, and from this, and the fact that the electronic structures of argon and chloride ion are similar, explained the great similarities between chlorides and cyanides. This followed from the similarities in the properties of argon and molecular nitrogen, and the notion that charged atoms or molecules, i.e., ions, should be alike, if uncharged atoms or molecules with the same architecture had the same properties. Another example of molecules with identical electronic structures is the pair CO_2, N_2O. These have almost identical physical properties and some very similar chemical ones, such as the formation of the hydrates $CO_2 \cdot 6H_2O$ and $N_2O \cdot 6H_2O$. The main difference is in their melting points: $-102°C$ for nitrous oxide and $-56°C$ for carbon dioxide. Langmuir points out that this difference is connected with a difference in molecular symmetry, and from this arrives at the structure $N = N = O$ for N_2O, similar in shape to, but not as symmetrical as, the structure $O = C = O$ for CO_2. (These structural formulas are now quite firmly established on the basis of many different sources of data).

Langmuir then defines atoms or molecules — whether charged or not — which have the same electronic arrangement as "isosteres" (Greek for "same

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structure"), and proceeds to write down isosteric sets: H^-, He, Li^+; $O^=$, F^-, Ne, Na^+, Mg^{++}, Al^{+++}; $S^=$, Cl^-, A, K^+, Ca^{++}; Cu^+, Zn^{++}; Br^-, Kr, Rb^+, Sr^{++}; Ag^+, Cd^{++}; I^-, Xe, Cs^+, Ba^{++}; N_2, CO, CN^-; CH_4, NH_4^+; CO_2, N_2O, N_3^-, CNO^-; NO_3^-, $CO_3^=$; NO_2^-, O_3^-; HF, OH^-; ClO_4^-, $SO_4^=$, $PO_4^{\equiv}$; ClO_3^-, $SO_3^=$, $PO_3^{\equiv}$; SO_3, PO_3^-; $S_2O_6^=$, $P_2O_6^{==}$; $S_2O_7^=$, $P_2O_7^{==}$; SiH_4^+, PH_4^+; MnO_4^-; $CrO_4^=$; $SeO_4^=$, $AsO_4^{\equiv}$. (The numbers of each set of isosteres are separated by comas, the different sets are separated by semicolons.)

Isosteres of equal charge should have very similar properties, and indeed they do, for example N_2O and CO_2, N_2 and CO, and N_3^- and NCO^-. To find data in support of the similarity of the structures of isosteres with different charges, Langmuir turned to crystallography.

A tremendous and accurate compendium of crystallographic data had been prepared by Groth[6] in which the symmetries, axial ratios, and other properties of all well described crystals were collected. Among these data Langmuir sought — and found — the correspondences for which he was looking. For instance: KCNO and KN_3 both crystallize in the tetragonal system with the axial ratios c/a of 0.5766 and 0.5798, respectively, and the crystals show similar face development and other properties. This similarity could hardly exist unless the shapes and force fields of the cyanate and trinitride ions were almost identical. Such a pair of crystals is called an "isomorphous" pair (Greek "same form"). Langmuir sought, and found, many other isomorphous sets of crystals, always in agreement with his notion of the isosterism of the ions or molecules of which the crystals were composed. Only a few of his examples will be mentioned here.

Sodium fluoride and magnesium oxide are crystals composed of isosteric ion pairs: Na^+, Mg^{++} and F^-, $O^=$. NaF and MgO should have the same crystal structure, and indeed they do. Bragg had shown that NaF has the now familiar face-centered cubic NaCl structure, and A. W. Hull soon showed (probably with Langmuir breathing down his neck) that MgO had the same, except that the interionic distances in MgO were shorter, as would be expected from the greater electrostatic charges holding the ions together.

(Langmuir was happy in the cubic arrangement of the ions in NaF and MgO, because he believed the Na^+, F^-, Mg^{++} and O^{--} ions were themselves cubic, each being enclosed by an octet of electrons vibrating about the positions of the vertices of a cube. We now believe, with considerable reason, that these ions are spherical, and that the cubic structures follow from the packing properties of spheres of different sizes and opposite charges. This change in viewpoint does not alter the general validity of the idea that isosteres should crystallize isomorphously.)

One of Langmuir's isomorphous pairs was $NaNO_3$ and $CaCO_3$. NO_3^- and $CO_3^=$ are isosteric and Na^+ and Ca^{++} should have nearly the same size, the extra positive charge on Ca^{++} decreasing the size of its noble gas electron

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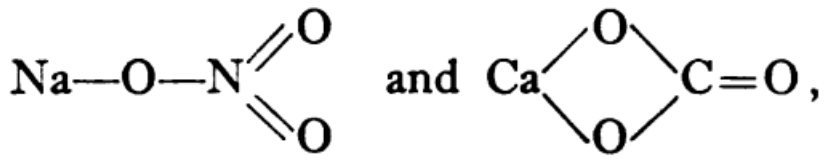
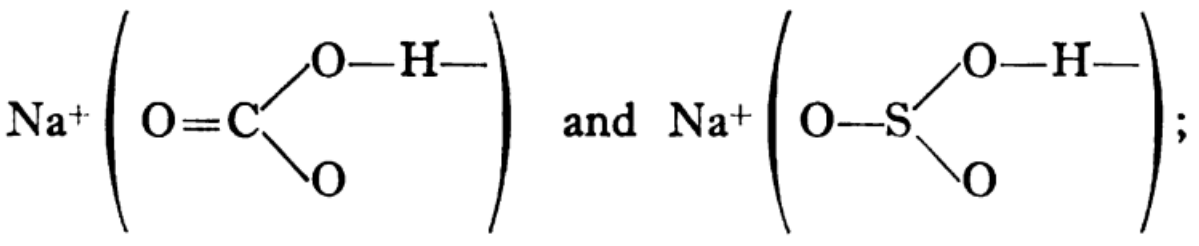
structure to nearly that of Na^+. The classical chemical structures of these were written



however, and these molecules could not have been similar in shape; on the other hand, the crystals of these two substances are both trigonal scalenohedral with c/a equal to 0.8297 and 0.8543, respectively, and both show similar optical properties and cleavage. Langmuir considered this sufficient proof of the formulas $(Na^+)(NO_3^-)$ and $(Ca^{++})(CO_3^{=})$, and subsequent determinations of the crystal structures of these substances have completely confirmed his reasoning.

In general, the crystallographers of those days — as of these — believed that isomorphism should occur among crystals composed of substances with similar chemical structures, but many of the chemical structures written in those days implied structural similarities which did not, in fact, exist. Much effort went into trying to show that crystals of, for instance, $NaHCO_3$ and $NaHSO_3$ were perhaps even a little isomorphous, although this is not so. It is true that $NaHCO_3$ and $NaHSO_3$ are both monoclinic, but the axial ratios and the interaxial angles are a:b:c = 0.7645:1:0. 3582, $\beta = 93°19'$ and a:b:c = 0.9276: 1:2. 2917, $\beta = 94°46'$. These crystals obviously have quite different internal atomic arrangements, and only the classical chemical formulae of the two compounds could lead one to hope for similar structures. Langmuir's and Lewis' formulation of these structures is



The anions in these substances would not be expected to have the same shape or force field, because the arrangement of the chemical bonds (shared electron pairs) in them is quite different; the carbon in carbonate is tetracovalent, the sulfur in sulfite is tricovalent. Langmuir considered a number of such examples culled from the classic crystallographic literature, and then told the crystallographers to look for isomorphism where *he* would expect it.

Modern crystal chemistry has built on this basis a vast body of knowledge, which has vindicated in almost every case the predictions made by Langmuir, both as to isomorphism and to the actual structures he predicted.

Langmuir's interest in the structures of crystals continued throughout his subsequent career. In 1920 he interested himself in the crystal structures of the ammonium halides[7] and deduced from the fact that NH_4Cl and NH_4Br

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have at low temperatures a structure in which each NH_4^+ is surrounded by eight equidistant Cl^- or Br^- ions at the corners of a cube that the NH_4^+ ion must be tetrahedral (as he expected from its being isosteric with CH_4); from the fact that these substances have a different structure at high temperatures in which each ion is surrounded by six equidistant ions of the opposite kind at the corners of a regular octahedron, he deduced that under these conditions the halide ions dominated the structure through the influence of their cubic octets of electrons. We would say now that the first of these conclusions is still valid, but that the second — concerning the high temperature forms of NH_4Cl and NH_4Br — should be modified. It is now thought that the thermal rotational motion of the NH_4^+ ions makes them effectively spherical at high temperatures, and that the structures of these halides is then determined by the packing of equal numbers of spheres of unequal sizes and opposite charges.

Much later, Langmuir published a paper with Dorothy Wrinch[8] on the interpretation of the vector map of the projection of an insulin crystal published by Dorothy Crowfoot of Oxford in that same year. Dorothy Wrinch had deduced from certain assumptions about the chemistry of peptides, and from geometrical considerations, a theory for the structures of proteins which has become less and less plausible as crystallographic and other data have been collected from proteins. One would say now (1960) that Wrinch's protein structures cannot correspond to those of any protein yet studied, but in those exciting days there were very few data, and Langmuir was fascinated by the new methods of interpreting the vector maps which can be constructed from the X-ray diffraction effects produced by crystals. Certainly, the interpretation Langmuir and Wrinch gave to the insulin vector map was justified, but it did not — and could not — define the insulin structure (which still remains unknown).

Having satisfied himself as to the principles on which the structures of atoms and molecules were built, Langmuir returned to his examination of the physical consequences of these structures. In fact, even before the publication of his famous paper on the electronic structures of atoms and molecules, he had been explaining the properties of substances in terms of the structures of the molecules in them. In doing this he used some arbitrary assumptions of his own devising, but he did not allow himself to change his assumptions from one problem to the next, and accordingly used considerable care in setting up these assumptions. They seem to have been justified by the wide range of phenomena which he was able to explain by their use.

To a chemist, like the present writer, Langmuir's assumptions seem reasonable enough. They are:

(1) The forces between ions and dipoles obey the ordinary laws of electrostatics, including the effect of the dielectric constant of the medium in which the ions or dipoles are suspended.

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(2) The force between molecules in contact can be considered as caused by a surface energy proportional to the area over which the molecules are in contact.

It is this second assumption that is Langmuir's own and which he used with so much skill and effectiveness in explaining and relating the properties of many chemical substances. He justifies it in a long review paper[9], and points out situations where it must be used with care, but in other papers he uses this assumption almost, or completely, without comment. It works very well.

As an example, consider the first case treated in Langmuir's article "The Distribution and Orientation of Molecules."[10] The substance is methanol, CH_3OH, with a volume per molecule of 67A°[3]. Assuming the molecules to be close-packed spheres, the surface area of a molecule turns out to be 65A°[2] and its diameter to be 4.56A°. Taking half the area to be methyl surface and the other half hydroxyl surface, each kind of surface has an area of 32A°[2]. Calling the hydrocarbon half of the molecule R and the hydroxyl half X, consider one methyl alcohol molecule at the surface of liquid methanol. There are two extreme orientations: the hemisphere X is submerged, or the hemisphere R is submerged. Let S be the surface area of the molecule, γ_R and γ_X the surface energies of R and X, respectively, and γ_{RX} the energy of the interface between R and X (all per unit area). In the first orientation the total surface energy is $1/2S(\gamma_X+1/2\gamma_{RX})$, and in the second orientation it is $1/2S(\gamma_X+1/2\gamma_{RX})$, if we assume the liquid touching the molecule in question to be randomly oriented and to present either R or X at random to the submerged surface of our molecule. The energy difference between these two orientations is $1/2S(\gamma_X-\gamma_R)$. The relative probabilities of these two orientations can now be computed from the Boltzmann equation:

$$\frac{P_1}{P_2}=\frac{p_1}{p_2}e^{\frac{\lambda}{kT}}$$

where P_1 and P_2 are the relative probabilities of the two states of the system (orientations, in this case), p_1 and p_2 are the so called *a priori* probabilities, i.e., the relative probabilities if energy effects are ignored, λ is the energy emitted by the system in going from state 1 to state 2, T is the absolute temperature, and k is the "Boltzmann Constant," equal to 1.372×10^{-16} erg/degree.

The surface energy* of hydrocarbons is close to 50 ergs/cm² and that of water is 117 ergs/cm². It is probable (says Langmuir) that the surface energy of pure hydroxyl is larger than that of water, because water molecules, too, are oriented at a water surface, so that γ_X may be reasonably taken to be about 190 ergs/cm². Then $\lambda=22\times10^{-14}$ or 46×10^{-14}, depending on which value of γ_X is assumed.

* The surface energy is given by $\gamma=\gamma_F-T^{d\gamma}F/dT$, where γ_F is the surface free energy ordinarily measured as surface tension.

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The Boltzmann equation gives from these data that $P_1/P_2 = 300$ or 100,000 (depending on the value of γ_x), assuming the *a priori* probabilities of the two orientations equal, and the temperature to be 20°C = 293°K. Thus the odds against finding the hydroxyl end of a methanol molecule sticking up through the surface of liquid methanol are between 300 to 1 and 100,000 to 1. Consequently, the surface of liquid methyl alcohol is essentially a hydrocarbon surface.

This example is typical of Langmuir's way of attacking a problem. Note the simplicity of method, the attention to detail, and the use of the most appropriate classical tools; note also the absence of extraneous material, and the selection of the most pertinent data. In the example just given, he wishes to know how the molecules are oriented in a liquid methanol surface, and proceeds to find his answer in the most efficient way.

Using arguments of the same kind as those in the example, but of course in a somewhat more involved way, Langmuir was able to show that the vapor pressures of organic liquids indicated that the molecules in the vapors were curled up so as to bury the active groups (hydroxyl, carboxyl, etc.) beneath a layer of hydrocarbon, whenever the molecule was large enough for such folding to be possible. This conclusion followed from a discrepancy between the vapor pressures calculated without the folding and the experimental facts. The calculated vapor pressures were too low, so that an increased stability for the vapor molecules had to be accounted for. This increased stability could be found in the surface energy of contact between different parts of the same molecule.

These successes encouraged Langmuir to work on the vapor pressure of brinary mixtures of organic compounds, then on their energies of mixing and subsequently on the mutual solubilities of liquids. Always using the same types of reasoning, he was able to explain most of the phenomena displayed by these systems, including the fact that water retains a small solubility in even long-chain hydrocarbons, although the hydrocarbons, and other long-chain aliphatic substances, become essentially insoluble in water as the chain length increases.

The excellent agreement between the results of this theory of "independent surface action", as Langmuir called it, and the experimental data led him to apply the same kind of reasoning to the behavior of long chain fatty acids on water surfaces. This subject fascinated Langmuir for many years, and is the subject of a chapter of its own in the next volume of this work.

By 1938 the world of chemistry was full of thoughts, theories, and experiments having to do with large molecules: high polymers held (and still hold) the attention of organic chemists, globular proteins were under study, and colloid phenomena were being actively worked on. Some remarkable behavior of suspensions of huge molecules (or, from another point of view, submicroscopic particles) in salt solutions came under Langmuir's eye, and imme-

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diately he set out to explain these phenomena on the basis of his point of view.

Several different suspensions: of tobacco mosaic virus, of ferric oxide, of vanadium pentoxide, of bentonite (a kind of clay), and of many other particulate substances show the phenomenon called "coacervation". For instance, a suspension in water of only two per cent of bentonite particles about 300A° in diameter separates on standing into two distinct phases. The less dense upper phase is optically isotropic, i.e., does not rotate the plane of polarized light, but the slightly more dense lower phase consists of apparently crystalline grains which are optically anisotropic and show up, when viewed between crossed polaroids, as a fine grained patchwork of many interference colors. The optic axes of these tiny anisotropic regions seemed to be inclined at about 45° to the axis of the sealed-off test tube in which the suspension was standing. Under mild forces, such as gently tilting the tube, the dense phase acted quite like a solid, but when the tube was shaken the whole contents of the tube behaved like a rather ordinary liquid.

Langmuir's enquiring mind could not resist such a problem. He procured some of this bentonite suspension, and had it made up into various concentrations. He observed it under flow and after standing. He shook it and watched the process of its return to equilibrium. He inverted the tubes and watched the air bubbles rise, or fail to rise, through the suspensions of invisible clay particles. He called on everyone who stepped into his laboratory to admire these remarkable sights, and deluged these visitors with theories, reports of observations, and questions. (I, the writer of this chapter, was one of these visitors. It was a stimulating, and somewhat exhausting experience to meet Langmuir armed with his bentonite suspensions. Indeed, it was almost always the same kind of experience, whether the armament consisted of bentonite, tungsten wire, proteins, water waves, clouds, crystals, or any other material objects which had unexplained behavior.)

It was clear immediately that the individual particles in such suspensions must be separated by dozens or hundreds of Angstrom Units of suspending medium — water containing very dilute ions. A perusal of the literature showed that various distinguished authors had given various explanations of the equilibrium of forces which could hold the suspended particles so almost rigidly in position with respect to one another through such great distances. It had been found that the particles were all charged electrically with the same sign, and it was the repulsion between these like charges which held the particles apart. But what held them together over such long distances? The experts had agreed that it must be the Van der Waals forces. How else could one explain the separation into two phases?

Langmuir was disdainful of this explanation, since Van der Waals forces were well known to act over only an Angstrom or so from molecular surfaces. Instead, he proposed that the situation was much the same as that in the crystal

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of a metal, in which ions of metallic atoms are suspended in a sea of mobile electrons. The ions repel one another, but attract the electrons which swim between them; the electrons attract the ions and repel one another; the result is that the neigh borhood of any ion is composed of electrons, but that enough other ions are not too far away to attract the electrons and keep them from forcing one another away into space. No Van der Waals forces here, only ordinary electrostatics! Langmuir imagined the charged bentonite particles to attract the oppositely charged mother liquid (water with enough excess ions of the correct charge). This force tends to bring the particles closer together and to squeeze out the mother liquor from between them, until the mutual repulsion of the similarly charged particles prevents their moving closer together. This balance of forces explains the existence of the dense phase — the dilute phase is what is left. All these phenomena are strongly affected by the thermal motion of the molecules of the mother liquor, the ions, and the charged, suspended particles themselves, and the various energies are related to the states of motion by the Boltzmann Equation, which Langmuir never forgets to use.

The bentonite particles are known to be thin, disc-like objects. Consequently, the orientation of one of the particles will affect the orientations of its neighbors; they all tend to be parallel, because of their mutual electrostatic repulsion. Thermal motion, on the other hand, tends to randomize their orientations. Viscous flow of the suspending medium will tend to align the particles parallel to the shear planes of flow. The combination of all these forces and motions must be responsible for the phenomena observed.

In an article on "The Role of Attractive and Repulsive Forces in the Formation of Tactoids, Thixtropic Gels, Protein Crystals, and Coacervates"[11] Langmuir discusses these problems, and gives somewhat qualitative mathematical descriptions of the behaviors of these various suspensions of particles in liquids. (The exact mathematical treatment of such a complex situation is, he says, extremely involved. It must be, nobody has carried out this treatment yet.) It is interesting how his point of view leads one almost automatically to predict the qualitatively correct result, whether the particles be platelets — bentonite, fibers—vanadium pentoxide or tobacco mosaic virus, or more or less spherical — globular protein molecules. Of these last he says "protein crystals are essentially coacervates."

If a small amount of one phase is surrounded by another, isotropic, phase, the surrounded region is normally spherical — a droplet of oil suspended in water, for instance — but if the surrounded region is not isotropic, it may not be spherical. The separation into two phases of freshly disturbed suspensions of bentonite, tobacco mosaic virus, etc., takes place by the formation of "tactoids"—spindle shaped droplets of the light phase in the dense one, and of the dense phase in the light one — which move in the upward or downward directions until they coalesce to form large bodies of light and dense phases. The

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shape of these tactoids is determined by the mutual orientation of the suspended particles in the dense phase; they are aligned with respect to one another, and so have low surface energy in some directions and high in others. The curvatures of the surfaces of these tactoids vary from point to point over their surfaces, in accordance with the orientations of the suspended particles just below the surface, and the result is the spindle shape. The points of the spindle are in the directions of edges or ends of suspended particles, the equatorial regions—"bellies"—of the spindles are bounded by the flat sides or lengths of the particles. Other shaped droplets occur during phase separations in other suspended systems. Langmuir spends few words on these interesting objects in his articles, but I have heard many impromptu lectures about them from him. Just as in all other cases, his concentration on the problem at hand, his use of all available knowledge, and his refusal to dismiss a problem until it had been solved (or, very rarely, proved insoluble) have given me an ideal of how a great scientist works, and have also given me guidance in attacking my own scientific problems; guidance, I must admit, sometimes difficult to follow.

My Debt to Irving Langmuir

In 1949 I had just been made head of a division of the Research Laboratory of the General Electric Company—the Crystallography Division—and was having a fine time in my first genuinely executive position. One of the privileges of the position was that of being invited to parties given by the directorate of the Laboratory, and that winter a very important such party occurred, one in honor of Drs. Coolidge, Hull, Dushman, and Langmuir, all of whom were retiring from their active positions in the Laboratory. Langmuir had been away for some time recovering from a cataract operation, and his appearance at this party was his first outing since entering the hospital.

During the cocktail hour I wandered over to greet Langmuir, to congratulate him on his recovery, and to listen to his experiences with his new, clear eyes. I was sure that he would be full of interesting observations and deductions—optical effects, colors, sensations would all be changed from before the cataracts were removed. But this was not what he talked about. His first remark was a question:

"If you had a million dollars, what would you do?"

I had, as it happened, considered this question for myself several times and had come to a conclusion. Before I had time to examine the effects of my answer, I made it:

"I would take ten years off and find the structure of a protein."

Langmuir said something like, "Hmm, sounds reasonable," and we were soon separated by other guests. Martinis were downed, dinner was consumed, and, after some speeches suitable to the occasion, we all went home.

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Two or three weeks later Langmuir came bouncing in to my beautiful new office and asked, "Did you mean what you said the other night? If you did, I think we can swing it!"

I was amazed and thrilled. I thought over my wishes and capabilities. The difference between the contemplation of a day dream, and the possibility of a practical reality was suddenly very apparent. I told Langmuir I would let him know in a day or two, and went to talk this wonderful opportunity over with my wife. We decided to accept, if the arrangements were practical. I told Langmuir I would do it, if the money was really available, and if the organizational and scientific arrangements were such as to make it possible to carry out a structure determination on so complex a molecule as a protein.

Langmuir said all this could be arranged. He had made contact with a very wealthy person who could be convinced to support all the necessary arrangements. This contact had been made through his brother, Dean Langmuir, who had been a lawyer and had been in touch with several charitable foundations and their supporters. Dean Langmuir had been discussing the disposition of a large sum of money this wealthy person wished to donate to some worthy cause and had apparently told his brother Irving about these discussion and asked his advice. Dean Langmuir then died. Irving Langmuir continued the negotiations with the prospective donor. I am still not sure about the details of this bit of history, because of the donor's insistence on anonymity and his desire to maintain it.

In any event, the result of the negotiations was the creation of a small foundation which was eventually called the "Dean Langmuir Foundation" with offices in New York City, and with the purpose of supporting research into the molecular structure of proteins. I was given the commission of finding a suitable place to work and of estimating the total amount of money required. It turned out that the Foundation could not provide enough money for an attack on such a problem. When Irving Langmuir learned of this, he immediately made an appointment for me with Warren Weaver of the Rockefeller Foundation, and went with me to meet him. The eventual result was that I established myself at the Polytechnic Institute of Brooklyn, as Director of the Protein Structure Project, an independent department of the Institute. This Project was established for ten years, starting July 1, 1950.

I worked at Brooklyn Poly for almost the ten years originally planned and collected a most competent and interesting staff. Together we learned many things about how to go about the problem of finding the molecular arrangement in a protein, but we still have not found it.

Late in 1959, I was offered the opportunity to become head of the Biophysics Department of the Roswell Park Memorial Institute in Buffalo, New York, and to bring my problem, my staff, and my equipment with me. I accepted this offer and have now just completed setting up a laboratory to continue this fascinating work.

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During his life, Irving Langmuir maintained his interest in our work and, when he visited us, always was full of encouragement and valuable suggestions and criticisms. Thus I owe to him my whole scientific career since 1950, a debt I can never repay to him, but which I can liquidate to some extent by successfully completing my structure determination of a protein molecule. This I intend to do. When it is finished, I plan to dedicate it to the memory of Irving Langmuir, a great scientist and a great friend.

DAVID HARKER

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PART 1

ATOMIC STRUCTURE

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THE STRUCTURE OF ATOMS AND THE OCTET THEORY OF VALENCE

Proceedings of the National Academy of Science
Vol. V, 252 (1919).

IN A PAPER soon to be published in the *Journal of the American Chemical Society*, I will give a new theory of the structure of atoms and molecules based upon chemical data. This theory, which assumes an atom of the Rutherford type, and is essentially an extension of Lewis' theory of the "cubical atom,"[1] may be most concisely stated in terms of the following postulates.

1. The electrons in atoms are either stationary or rotate, revolve or oscillate about definite positions in the atom. The electrons in the most stable atoms, namely, those of the inert gases, have positions symmetrical with respect to a plane called the equatorial plane, passing through the nucleus at the center of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) perpendicular to the equatorial plane through which four secondary planes of symmetry pass, forming angles of 45° with each other. These atoms thus have the symmetry of a tetragonal crystal.

2. The electrons in any given atom are distributed through a series of concentric (nearly) spherical shells, all of equal thickness. Thus the mean radii of the shells form an arithmetric series 1, 2, 3, 4, and the effective areas are in the ratios $1:2^2:3^2:4^2$.

3. Each shell is divided into cellular spaces or cells occupying equal areas in their respective shells and distributed over the surface of the shells according to the symmetry required by postulate 1. The first shell thus contains 2 cells, the second 8, the third 18, and the fourth 32.

4. Each of the cells in the first shell can contain only one electron, but each other cell can contain either one or two. All the inner shells must have their full quotas of electrons before the outside shell can contain any. No cell in the outside layer can contain two electrons until all the other cells in this layer contain at least one.

5. When the number of electrons in the outside layer is small, these electrons arrange themselves over the underlying ones, being acted on by magnetic attractive forces. But as the charge on the kernel or the number of electrons in the outside layer increases, the electrostatic repulsion of the underlying

[1] Lewis, G. N., *J. Am. Chem. Soc.* **38**, 1916 (762–785).

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electrons becomes predominant and the outer electrons then tend to rearrange themselves so as to be as far as possible from the underlying ones.

6. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by: (*a*) a single nucleus; (*b*) two hydrogen nuclei; (*c*) a hydrogen nucleus and the kernel of another atom; (*d*) two atomic kernels (very rare).

7. The next most stable arrangement of electrons is the octet; that is, a group of eight electrons like that in the second shell of the neon atom. Any atom with atomic number less than twenty, and which has more than three electrons in its outside layer tends to take up enough electrons to complete its octet.

8. Two octets may hold one, two, or sometimes three pairs of electrons in common. One octet may share one, two, three or four pairs of its electrons with one, two, three or four other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets.

The inert gases are those having atoms in which all the cells in the outside shell have equal numbers of electrons. Thus according to the first four postulates the atomic numbers of the inert gases should be 2, 10, 18, 36, 54, and 86 in agreement with fact.

All atoms with an atomic number greater than that of helium, have as their first shell a pair of electrons close to the nucleus. The line connecting the two electrons establishes the polar axis for the atom. Neon has in its second shell eight electrons, four in each hemisphere (i.e., above and below the equatorial plane), arranged symmetrically about the polar axis. The eight electrons are thus nearly at the corners of a cube. In argon there are eight more electrons in the second shell.

The eight electrons in the third shell of the atom of iron are arranged over the underlying electrons in the second shell. The two extra electrons in the atom of nickel are placed in the polar axis. Beyond nickel the electrons in the atom cannot be held by magnetic forces, and thus tend to rearrange themselves so as to be placed as far as possible from the underlying electrons. This leads to an explanation of the chemical and magnetic properties of copper, zinc, etc.

Krypton has in its third shell nine electrons in each hemisphere, symmetrically placed with respect to the polar axis and to the four electrons in the second shell. The ninth electron in each hemisphere goes into the polar axis. Xenon is like krypton, except that it has twice as many electrons in its third shell. Beyond Xenon eighteen electrons in the fourth shell can be held by magnetic forces over the eighteen cells of the third shell, so that lutecium, the eighteenth element beyond Xenon marks the last of the rare earth elements. The electrons in the outside shell of the atoms beyond this element are arranged as far as possible so as to leave eighteen empty spaces over the underlying electrons.

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In this way it is possible to explain the chemical and magnetic properties of tantallum and tungsten as contrasted to those of the rare earths.

Niton has sixteen electrons in each hemisphere of its fourth shell. These are placed symmetrically with respect to the polar axis and the eight underlying electrons.

This theory of atomic structure explains in a satisfactory way most of the periodic properties of all the elements including those of the eighth group and the rare earths. It lends itself especially well to the explanation of the so-called physical properties, such as boiling-points, freezing-points, electric conductivity, etc. For the details of its application to specific elements the paper in the *Journal of the American Chemical Society* should be consulted.

Postulates 6, 7 and 8 lead directly to a new theory of valence which we may call the Octet Theory. This theory may be stated in terms of the equation

$$e = 8n - 2p \qquad (1)$$

where e is the total number of available electrons in the shells of all the atoms in a molecule; n is the number of octets forming the outside shells of the atoms and p is the number of pairs of electrons held in common by the octets (Postulate 8). If we let E be the number of electrons in the "shell" of an atom then $e = \Sigma(E)$. The value of E for a given atom, at least in case of the first twenty elements, corresponds to the ordinal number of its group in the periodic table. Thus we have the following values of E:— one for hydrogen, lithium, sodium, etc., two for magnesium, three for boron, aluminum, etc.; four for carbon and silicon, five for nitrogen and phosphorus; six for oxygen and sulphur; seven for the halogens, and zero for the inert gases.

The above equation expresses the fact that every pair of electrons held in common between two octets results in a decrease in two in the total number of electrons needed to form the shells of the atoms in the molecules. It also implicitly expresses the fact that *all the electrons* in the shells of the atoms forming a molecule form part of one or two of the octets in the molecule.

It seems that this simple equation is a practically complete statement of a theory of valence that applies with very few exceptions to all compounds formed from the first twenty elements. With some modifications it applies also to most compounds of other elements. In the case of organic compounds it is found that each pair of electrons held in common between atoms corresponds exactly to the valence bond used in the ordinary theory of valence. It is therefore proposed to define valence as the number of pairs of electrons which a given atom shares with others. In view of the fact known that valence is very often used to express something quite different, it is recommended that the word *covalence* be used to denote valence defined as above.

Equation (1) expresses the fact that the number of covalence bonds in a molecule must be related to the number of available electrons in the molecule.

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A simple mathematical analysis[3] shows that all structural formulas written according to the ordinary valence theory in which the valence for each element is taken equal to 8-E, will satisfy Equation (1). Thus the Octet Theory requires no modification in any formula written with the following valencies; carbon-four, nitrogen-three; oxygen-two; chlorine-one and hydrogen-one. In some cases, however, the Octet Theory suggests that other formulas besides those usually adopted may be possible. Whenever the old theory of valence has assumed valencies other than those mentioned above, such as five for nitrogen or phosphorus; four or six for sulphur; three, five or seven for chlorine, etc., the Octet Theory gives quite different structural formulas from those usually assumed. This is readily seen when it is considered that the covalency of an element according to the Octet Theory can never exceed four, since there are only four pairs of electrons in an octet.

A careful examination of the cases showing a discrepancy between the old and new theories furnishes the strongest kind of evidence in support of the Octet Theory. The non-existence of such compounds as H_4S, H_6S, SCl_6, NCl_5, NH_5, etc., is in full accord with the theory as is also the existence of SO_2, SO_3, N_2O_5, HNO_3, NH_4Cl, etc. In these latter cases, however, the formulas written are different from those usually adopted. For example, the covalence of sulphur is three in SO_2, four in SO_3; that of nitrogen is four in N_2O_5, HNO_3, and NH_4Cl. These covalencies are, however, not *assumed* as in the ordinary valence theory, but are *derived* from Equation (1), which is the *same* equation as that which applies to all ordinary organic compounds. In a similar way it is found that the Octet Theory fully explains the structures of such compounds as N_2O, N_2O_3, N_2O_4, HN_3, $N(CH_3)_4Cl$, H_3PO_3, H_3PO_4, $HClO$, $HClO_2$, $HClO_3$, $HClO_4$, H_2O_2, and even so-called complex compounds such as $B(CH_3)_3$, NH_3, $K_2PtCl_2.2NH_3$, KBF_4, Na_2S_5, etc.

From this viewpoint a very large number of compounds previously considered by Werner are found to be typical primary valence compounds not essentially different in their structures from organic compounds. It is especially significant that the structure of these compounds is found from Equation (1), without any additional assumptions. Thus we are lead to a *single theory* of valence which explains and coördinates the separate valence theories that we have needed in the past.

There are many facts not previously well understood which are very readily explained by the new theory. For example, the fact that we have weak and strong acids, weak and strong bases, but no "weak" and "strong" salts, is automatically explained.

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[3] This will be published in full in a paper soon to be submitted to the *Journal of the American Chemical Society*. This second paper will deal in some detail with the application of the Octet Theory to organic chemistry, particularly to nitrogen, sulphur, compounds, etc. The stereoisomerism of such compounds will be discussed.

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The theory indicates that all salts consist of negative and positive ions even when in the solid condition, and that no pair of electrons are held in common between the negative and positive groups. Thus in sodium chloride the covalence of both sodium and chlorine is zero, and this fact explains the non-existence of molecules of sodium chloride shown by the X-ray crystal analysis. When sodium chloride is dissolved in water the water does not cause ionization, but simply causes the separation of atoms already ionized. This direct result of the Octet Theory is in full accord with experiment and with Milner's recent theory of strong electrolytes. *London, Phil. Mag.*, **35**, 1918 (214, 354).

In the field of organic compounds the theory fits the facts particularly well. Although in the case of compounds like SF_6, H_2SiF_6, etc., there is very definite evidence that the *kernels* of the atoms of sulphur and silicon are cubical in shape, there is the strongest evidence that in organic compounds the carbon atom has the eight electrons of its octet drawn together into four pairs, arranged at the corners of a tetrahedron. This is in full accord with the fact that in SF_6, and H_2SiF_6, the central atom has given up electrons to the surrounding atoms, so that the cubical kernels do not share any electrons with the other atoms, while in organic compounds the carbon atoms always share four pairs of electrons with adjacent atoms. From this we must conclude that a pair of electrons held in common by two octets acts as if it were located at a point between the two atoms. This conclusion, which can be reduced from the properties of a very few simple organic compounds is found to apply apparently without exception to compounds of nitrogen, sulphur, phosphorus, and even cobalt compounds, etc. It seems to explain all the cases of stereoisomerism that I am familiar with. For example, in the amine oxides, $NR_1R_2R_3O$, nitrogen is quadricovalent, so that these substances exist as optical isomers, just as in the case of a carbon atom attached to form different groups.

The isomerism of compounds of tervalent nitrogen such as ketoximes, hydrazones, ozazones, and diazo-compounds, etc., is readily accounted for, as well as the absence of isomers among tertrary amines, etc. Not only are the substituted ammonium compounds fully explained, but also the sulfonium, phosphonium, and oxonium compounds. Thus the structures of $S(CH_3)_3OH$, $S(CH_3)_4Cl_2$, $(C_2H_5)_2O.HCl$, etc., are readily found from the Octet Theory and their salt-like character is explained. The covalence of the central atom in the above compounds is three, four and three respectively.

When the values of e and n are both the same for two or more compounds it is evident according to the Octet Theory that these may have practically identical structures. An example of this kind is found in N_2 and CO. The total number of electrons in each molecule (including those in their kernels) is fourteen. Evidence is given in the paper in the *Journal of the American Chemical Society* that the structures of these two molecules is identical, except for the fact that in one case there are two nuclei of seven positive charges each, while in the other there are nuclei of six and eight charges, respectively. These mole-

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cules are, however, exceptional, in that the molecule consists of a *single octet* arranged around a complex kernel.

Another example of a pair of compounds which according to the Octet Theory should have similar structures occurs in the case of CO_2 and N_2O. For each of these molecules $n = 3$, $e = 16$ and therefore $p = 4$. The best method of testing this conclusion lies in comparing the "*physical*" properties of the two substances. The "chemical" properties depend primarily on the ease with which the molecules can be broken up, and thus is a measure of the internal forces within the molecule, which depend to a large extent on the charges on the kernels. The so-called "physical" properties on the other hand depend on the stray field of force outside of the molecule, and this naturally depends rather on the arrangement of the outside electrons.

As a matter of fact we find that most of the physical properties of these two gases are practically identical.

The following data taken from Landolt-Börnstein tables and Abegg's hand book illustrate this.

	N_2O	CO_2
Critical pressures	75	77 atmos.
Critical temperatures	35.4°	31.9°
Viscosity at 20°C	148×10^{-6}	148×10^{-6}
Heat Conductivity at 100°C	0.0506	0.0506
Density of Liquid at −20°	0.996	1.031
Density of Liquid at +10°	0.856	0.858
Refractive index of liquid. D line, 16°C	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atmos. 16°C	0.12×10^{-6}	0.12×10^{-6}
Solubility in water 0°	1.305	1.780
Solubility in alcohol at 15°	3.25	3.13

Both gases from hydrates $N_2O.6H_2O$ and $CO_2.6H_2O$. The vapor pressure of the hydrate of N_2O is 5 atmospheres at −6°C while the hydrate of CO_2 has this vapor pressure at −9°C. The heats of formation of the two hydrates are given respectively as 14,900 and 15,000 calories per gram molecule.

The surface tension of liquid N_2O is 2.9 dynes per cm at 12.2°, while CO_2 has this same surface tension at 9.0°.

Thus N_2O at any given temperature has properties practically identical with those of CO_2 at a temperature 3° lower.

These results establish the similarity of outside structure of the molecules.

There is one property however, which is in marked contrast to those given above. The freezing-point of N_2O is −102° while that of CO_2 is −56°. This fact may be taken as an indication that the freezing-point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of CO_2 is slightly more symmetrical, and

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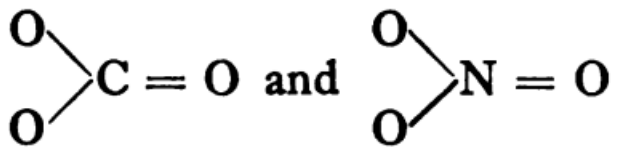
has a slightly weaker external field of force than that of N_2O. Such differences could easily be produced by the difference in the charges on the kernels.

There are many other examples of compounds having similarly formed molecules. It will be convenient to call these *isosteric compounds* or *isosteres.* These may be defined as compounds whose molecules have the same number and arrangement of electrons.

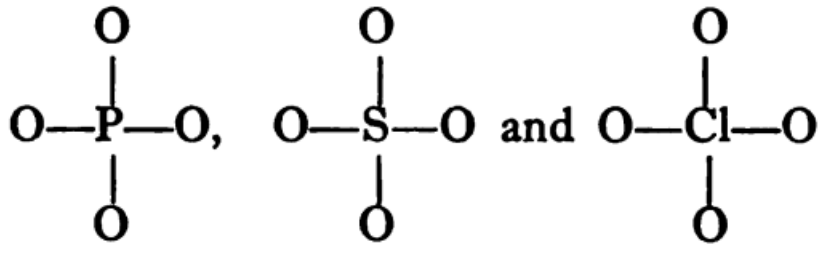
Another example of a pair of isosteres is that of HN_3 and HCNO. The similarity of properties should be most marked in the salts of these acids. The available data on solubilities and crystalline form seem to show that the salts of these two acids are very closely similar in physical properties.

This relationship of compounds may be carried much further. Thus, according to the Octet Theory, we should regard CH_4 as an isostere of the NH_4 ion. The electric charge on the ion prevents a direct comparison of physical properties. Other examples are:

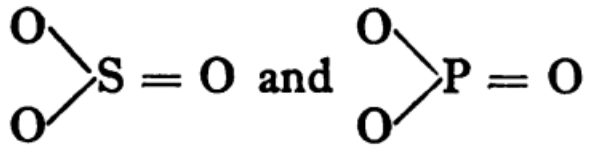
The carbonate and nitrate ions:



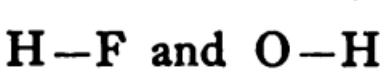
The orthophosphate, sulphate and perchlorate ions:



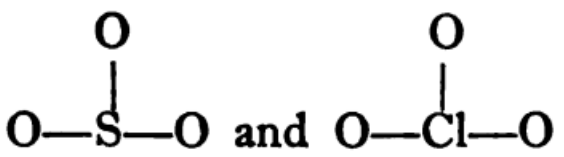
Sulfur trioxide and the metaphosphate ion:



The hydrofluoric acid molecule and the hydroxyl ion:



The sulfite and the chlorate ions:



We may attribute the differences in physical properties in all these cases to the effect of the differences in the electric charges.

Lewis has already pointed out that a theory of the kind outlined in this paper explains satisfactorily the facts which have led many chemists to assume polar valence. For example, the chlorine atom in chlor-acetic acid, because of the relatively large charge on its kernel, as compared for example with a carbon atom, tends to displace towards itself the electrons holding it

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to the carbon atom. This effect is transmitted with gradually decreasing intensity to the further end of the molecule, where it results in drawing the pair of electrons which holds the hydrogen nucleus to the octet of the oxygen atom, away from the hydrogen nucleus. Another way of looking at the effect is to consider that the positive kernel of the oxygen atom is displaced toward the hydrogen nucleus, and thus tends to weaken the force holding it. This effect makes it easier for the hydrogen nucleus to separate from the rest of the molecule as a positive ion. It is felt that this explanation can be applied in general to explain nearly all cases where polar valence bonds have been assumed in the past. This question will be discussed in more detail in the second paper to be published in the *Journal of the American Chemical Society*.

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THE ARRANGEMENT OF ELECTRONS IN ATOMS AND MOLECULES

Journal of the American Chemical Society
Vol. XLI, No. 6, June (1919).

THE PROBLEM of the structure of atoms has been attacked mainly by physicists who have given little consideration to the chemical properties which must ultimately be explained by a theory of atomic structure. The vast store of knowledge of chemical properties and relationships, such as is summarized by the Periodic Table, should serve as a better foundation for a theory of atomic structure than the relatively meager experimental data along purely physical lines.

Kossel[1] and Lewis[2] have had marked success in attacking the problem in this way. The present paper aims to develop and somewhat modify these theories. Lewis, rejecting the physical data as being insufficient or inconclusive, reasons from chemical facts that the electrons in atoms are normally stationary in position. These electrons arrange themselves in a series of concentric shells, the first shell containing two electrons, while all other shells tend to hold eight. The outermost shell however may hold 2, 4, or 6, instead of 8. The 8 electrons in a shell are supposed to be placed symmetrically at the corners of a cube or in pairs at the corners of a regular tetrahedron. When atoms combine they usually hold some of their outer electrons in common, two electrons being thus held for each chemical bond. These electrons may form parts of both atomic shells of 8 electrons. By means of these postulates Lewis is able to give an extraordinarily satisfactory explanation of the periodic arrangement of the elements and to explain in detail most of their chemical properties. He confines his attention, however, exclusively to the inert gases, the alkali and the alkaline earth metals, the halogens, boron, aluminium, scandium, carbon, silicon, nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulfur, selenium, and tellurium, a total of 35 out of the 88 known elements. The theory in its present form does not apply at all satisfactorily to any of the other elements.

[EDITOR'S NOTE: A brief excerpt of this paper was published in *J. Franklin Inst.* **187**, 359 (1919); also *Phys. Rev.* **13**, 300 (1919). Complete paper published *Gen. Elect. Rev.* **22**, 505, 587, 789 (1919).]

[1] W. Kossell, *Ann Physik.* **49**, 229 (1916).

[2] G. N. Lewis, *J. Am. Chem. Soc.* **38**, 762 (1916).

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Kossel's theory has many points of similarity. He conceives of the electrons as located in a plane in concentric rings, rotating in orbits about the nucleus. Certain arrangements, corresponding to those of the inert gases, are supposed to be of unusual stability and all the other atoms, in forming compounds tend to give up or take up electrons so that their electrons may become arranged like those of the inert gases. Kossel considers only the elements up to cerium, a total of 57. His theory does not satisfactorily account for the properties of the elements from vanadium to zinc or from columbium to silver and is only partially satisfactory for any of the elements above vanadium. In other words, its main success is limited to the first 23 elements. The theory does not lend itself nearly as well as that of Lewis to the detailed explanation of the properties of elements and their compounds. A rather thorough review and discussion of these and other recent theories of atomic structure has been published by S. Dushman.[1]

There is much chemical evidence, especially in the field of stereochemistry, that the primary valence forces between atoms act in directions nearly fixed with respect to each other. This can only be satisfactorily accounted for by electrons arranged in three dimensions.

Kossel attempts to explain the tetrahedral arrangement of the carbon valences by arguing that 4 spheres drawn in by strong forces towards a central atom must arrange themselves as a tetrahedron and that if the forces are great enough they will not be able to shift their positions. It is evident that even this structure would not have the requisite symmetry for the carbon atom, when the plane of the electron orbit is taken into account. But there is, moreover, conclusive evidence, even when carbon atoms are surrounded by less than 4 other atoms, that the forces act in definite directions. For example, if wood is carbonized under certain conditions a charcoal is obtained having about the same volume as the wood. This is notably true when such a substance as finely divided tungsten trioxide is reduced in very dry hydrogen. The volumes occupied are in some cases 20 or 25 times as great as that of the corresponding solid in crystalline form. The whole behavior of such bodies, especially in regard to their sintering at higher temperatures, indicates that the atoms are arranged in branching chains in which most atoms are surrounded by only two or three others. Since the bodies are definitely solid it must follow that the atoms are not able to shift their relative positions except when acted on by strong external forces. Such structures are inconceivable if atoms contain only electrons revolving in orbits about the nuclei.

Further evidence for the stationary electrons has been obtained by Hull who finds that the intensities of the lines in the X-ray spectra of crystals are best accounted for on the theory that the electrons occupy definite positions in the crystal lattice.

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[1] *Gen. Elect. Rev.* **20**, 186, 397 (1917).

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In attempting to determine the arrangement of electrons in atoms we must be guided by the numbers of electrons which make up the atoms of the inert gases; in other words by the atomic numbers of these elements, namely, helium 2, neon 10, argon 18, krypton 36, xenon 54, and niton 86.

Rydberg[1] has pointed out that these numbers are obtained from the series

$$N = 2(1+2^2+2^2+3^2+3^2+4^2+).$$

The factor two suggests a fundamental two-fold symmetry for all stable atoms. By a consideration of this equation and principles of symmetry and by constant checking against the Periodic Table and the specific properties of elements I have been led to the postulates given below. Some of these may seem in themselves to be very improbable and will undoubtedly need to be modified as more facts are acquired. But it is felt that all contain a fundamental basis of truth and that, although future modifications may make them take rather different forms, their application in predicting properties of elements will not be greatly altered.

The first postulate is concerned particularly with the structure of the stable atoms of the inert gases.

Postulate 1.—The electrons in the atoms of the inert gases are arranged about the nucleus in pairs symmetrically placed with respect to a plane passing through the nucleus which we may call the equatorial plane. The atoms are symmetrical with respect to a polar axis perpendicular to the plane and passing through the nucleus. They have also 4 secondary planes of symmetry passing through the polar axis and making 45° angles with each other. The symmetry thus corresponds to that of a tetragonal crystal. Since the electrons must occur in pairs symmetrical to the equational plane there are no electrons in this plane.

Postulate 2.—The electrons in the atoms are distributed through a series of concentric spherical[2] shells. All the shells in a given atom are of equal thickness. If the mean of the inner and outer radii be considered to be the effective radius of the shell then the radii of the different shells stand in the ratio 1:2:3:4, and the effective surfaces of the shells are in the ratio $1:2^2:3^2:4^2$.

Postulate 3.—Each spherical shell is divided into a number of cellular spaces. The thickness of these cells measured in a radial direction is equal to the thickness of the shell and is therefore the same (Postulate 2) for all the cells in the atom. In any given atom the cells occupy equal areas in their respective shells. All the cells in an atom have therefore equal volumes. The first postulate, regarding symmetry, applies also to the location of the cells. The first shell therefore contains two cells obtained by dividing the shell into two equal parts by the equatorial plane. The second shell having 4 times

[1] *Phil. Mag.* **28**, 144 (1914).

[2] In accordance with Postulate 1, it is probable that the surfaces of the shells are ellipoids of revolution rather than spheres. In the present argument this distinction is immateriall.

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the surface (Postulate 2) contains 8 cells. The third shell thus contains 18 while the fourth contains 32 cells. Or if we consider only one hemisphere the numbers in the successive shells are 1, 4, 9 and 16.

Postulate 4.—Each of the two innermost cells can contain only one electron[1] but each of the other cells is capable of holding two. There can be no electrons in the outside shell until all the inner shells contain their maximum numbers of electrons. In the outside shell two electrons can occupy a single cell only when all other cells contain at least one electron. We may assume that two electrons occupying the same cell are at different distances from the nucleus. Each shell, containing its full quota of electrons, thus consists of two "layers". We will find it convenient to refer to these layers of electrons by the symbols I, II*a*, II*b*, III*a*, III*b*, and IV*a* where the Roman numerals denote the shell containing the layer. Helium, neon, argon, krypton, or xenon, contains, respectively, the first 1, 2, 3, 4, or 5 of these layers, while niton contains all six.

The two-fold symmetry assumed in Postulate 1 is derived from the factor 2 which occurs in Rydberg's equation. The 4-fold symmetry is derived from the remarkable numerical relation brought out in the following table:

Shell	Radius	n	No. of cells	
			in axis	in zones
I	1	1	1	0
II	2	4	0	4
III	3	9	1	8
IV	4	16	0	16

Here n represents the number of cells in one of the hemispheres of the shell. If this number is odd one of the cells must lie along the polar axis; all other cells must be distributed in zones about this axis.

We see from this table that the number of cells which must be arranged in zones is always a multiple of 4. We can therefore assume tetragonal symmetry for the atoms of the inert gases.

Postulates 2 and 3 offer perhaps the simplest possible explanation of the occurrence of the terms 1, 2^2, 3^2 and 4^2, in Rydberg's relation. There are some reasons for believing that the shells close to the nucleus would lie closer together. These reasons are based mainly on the assumption that Coulomb's inverse square law holds even at short distances, and for this assumption there is little experimental evidence, except in the case of forces between two positive nuclei (Rutherford's scattering experiments). It is probable that the law of force is quite different for electrons bound in an atom and for positive or negative particles passing through the atom.

The assumption of the existence of cells independent of the electrons in them, seems to be needed to account for the properties of elements above

[1] If, as Rydberg believes, there are two undiscovered elements of atomic weights less than that of hydrogen, then this exception in the case of the innermost cells may be avoided.

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the rare earths. It is however closely related to Bohr's assumption of the existence of stationary states. The passage of an electron from one cell to another probably causes the emission of a spectrum line. It should be noted that the numbers 1, 2^2, 3^2, 4^2, etc., also occur in Bohr's theory in the determining of the location of the stationary orbits. It is probable that a common explanation will be found for both theories.

Postulate 4 seems necessary to take into account that the terms 2^2, 3^2, etc., in Rydberg's series occur twice. It seems to denote a remarkable tendency like that suggested by Postulate 1 for the electrons to form pairs.

From the steady progression in the properties of the different inert gases, however, we must conclude that the two electrons in a single cell do not exert very strong forces on each other.

The first 4 postulates give us a definite conception of the arrangement of the electrons in the atoms of the inert gases. Helium consists of two electrons symmetrically placed with respect to the nucleus. This same pair exists (as Shell I) in the atoms of all the other inert gases and determines the position of the polar axis. Neon contains a second shell (II*a*) containing 8 electrons arranged at the corners of two squares placed symmetrically with respect to the equatorial plane and parallel to it. These positions probably correspond fairly closely to the corners of a cube, but the effect of the two electrons in the first shell should be to shorten the cube in the direction of the polar axis. Argon is just like neon, except that there is a second layer of 8 electrons (II*b*) in the second shell. The two inner shells of krypton are like the two shells of argon, but in addition it has a third shell containing 18 electrons. Two of these electrons are located at the ends of the polar axis while the other 16 are placed symmetrically to the axis and to the equatorial plane and to the electrons in the inner shells. In all probability 4 of the 8 electrons in each hemisphere are located in the same plane as those in the second shell, while the other 4 are in planes making a 45° angle with these.

Xenon is like krypton except for the addition of another layer (III*b*) of electrons in the third shell.

Nitron has in addition to the 3 shells of xenon a fourth shell containing 32 electrons, 16 for each hemisphere. We have no data by which to determine the exact arrangement of these, but it is obvious that the 16 can be arranged with a high degree of symmetry with respect to the underlying layer of 8 electrons (in each hemisphere).

The following postulates deal with the forces and tendencies which govern the arrangement of electrons in the outside layer of atoms other than those of the inert gases:

Postulate 5.—It is assumed that electrons contained in the same cell are nearly without effect on each other. But the electrons in the outside layer tend to line themselves up (in a radial direction) with those of the underlying

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shell because of a magnetic field probably always to be associated with electrons bound in atoms. (Parson's magneton theory.) This attraction may be more or less counteracted by the electrostatic repulsion between the outside electrons and those in the underlying shell. The electrons in the outside layer also repel each other and thus tend to distribute themselves among the available cells so as to be as far apart as possible. The actual positions of equilibrium depend on a balance between these 3 sets of forces together with the attractive force exerted by the nucleus.

Postulate 6.—When the number of electrons in the outside layer is small, the magnetic attraction exerted by the electrons of the inner shells tends to predominate over the electrostatic repulsion, but when the atomic number and the number of electrons in the outside layer increase, the electrostatic forces gradually become the controlling factor. As a result, when there are few electrons in the outer layer these arrange themselves in the cells over those of the underlying shell, but where the outside layer begins to approach its full quota of electrons the cells over the underlying electrons tend to remain empty.

Postulate 7.—The properties of the atoms are determined by the number and arrangement of electrons in the outside layer and the ease with which they are able to revert to more stable forms by giving up or taking up electrons, or by sharing their outside electrons with atoms with which they combine. The tendencies to revert to the forms represented by the atoms of the inert gases are the strongest, but there are a few other forms of high symmetry such as those corresponding to certain possible forms of nickel, palladium, erbium and platinum atoms towards which atoms have a weaker tendency to revert (by giving up electrons only).

We may now apply these 7 postulate sto derive the properties of the chemical elements. We will first go through the list of elements dealing only with broad features and will later consider the properties of certain elements in more detail. At present we will confine our attention to the properties of the elements in atomic condition — we shall discuss only their tendencies to take up or give up electrons. The properties of the elements in solid or liquid form or in their compounds involve forces acting between different atoms and therefore can be best considered after we have discussed the formation of molecules. The properties of the atoms up to argon fit in well with even the older arrangements of the periodic table. In fact, the present theory and Lewis' theory resemble each other very closely as far as their application to these first 18 elements is concerned.

Table I to which it will be convenient to refer frequently during the following discussion, contains, a list of all the elements, arranged in order of their atomic numbers. The table is designed to show the way in which the electrons are arranged in the different shells. The numbers forming the first horizontal line denote the number of electrons in the outside layer of the

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TABLE I

Classification of the Elements According to the Arrangement of Their Electrons

Layer.	$NE = 0$		1	2	3	4	5	6	7	8	9	10
I			H	He								
II*a*	2	He	Li	Be	B	C	N	O	F	Ne		
II*b*	10	Ne	Na	Mg	Al	Si	P	S	Cl	A		
III*a*	18	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
			11	12	13	14	15	16	17	18		
III*a*	28	Niβ	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
III*b*	36	Kr	Rb	Sr	Y	Zr	Cb	Mo	43	Ru	Rh	Pd
			11	12	13	14	15	16	17	18		
III*b*	46	Pdβ	Ag	Cd	In	Sn	Sb	Te	I	Xe		
IV*a*	54	Xe	Cs	Ba	La	Ce	Pr	Nd	61	Sa	Eu	Gd
			11	12	13	14	15	16	17	18		
IV*a*			Tb	Ho	Dy	Er	Tm	Tm_2	Yb	Lu		
		14	15	16	17	18	19	20	21	22	23	24
IV*a*	68	Erβ	Tmβ	$Tm_2\beta$	Ybβ	Luβ	Ta	W	75	Os	Ir	Pt
			25	26	27	28	29	30	31	32		
IV*a*	78	Ptβ	Au	Hg	Tl	Pb	Bi	RaF	85	Nt		
IV*b*	86	Nt	87	Ra	Ac	Th	Ux_2	U				

atom. The first vertical column gives the index number of this outside layer. Thus boron has 3 electrons in the II*a* layer, chromium has 6 in the III*a* layer.

Hydrogen ($N = 1$) has a single electron. It is therefore (Postulates 1 and 7) unsaturated and tends to take up an electron in order to assume the symmetrical form characteristic of helium. The valence of hydrogen is therefore unity.

With helium ($N = 2$) the first shell is completed. Beyond this point any additional electrons must go into the first layer of the second shell (II*a*). There are 8 cells in this layer (Postulate 3) so that 8 electrons can be added before the atoms again acquire the stability of an inert gas. In lithium ($N = 3$) the single electron in the second shell is easily detached so that the atom reverts to the stable form that corresponds to helium, thus forming a univalent cation. In Fig. 1 the positive and negative valences of the elements are plotted against their atomic numbers.[1] It is seen that up to $N = 17$ the maximum positive valency increases regularly up to the halogens (with the exception of oxygen and fluorine). This maximum valency is determined

[1] This figure is taken with some modifications from I.W.D. Hackh. *J. Am. Chem. Soc.* **40**, 1024 (1918).

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by the number of electrons which are given up when the atom reverts to that of the next lower inert gas.

In beryllium and boron the properties are determined largely by the ability of the atom to revert to the form corresponding to helium. The actual arrangement of the electrons in the atoms of these elements is thus of little significance. In carbon the 4 electrons in the second shell tend to arrange themselves (Postulate 5) at the corners of a tetrahedron for in this way they can get as far apart as possible. With nitrogen no symmetrical arrange-

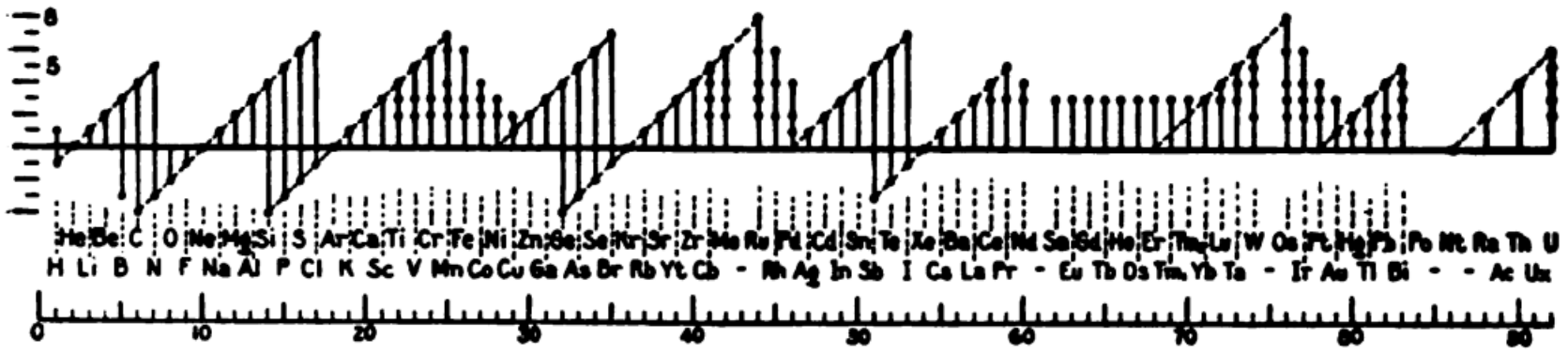

FIG. 1.

ment of the 5 electrons is possible. We shall see that this leads nitrogen to form a series of very unusual compounds. Whereas the properties of the elements from lithium up to carbon vary in a rather regular progression, the properties of carbon and nitrogen form a very sharp discontinuity. The constant valence of carbon — the variable valence of nitrogen; the high melting point of carbon — the low melting point of nitrogen; the very great inertness and stability of most carbon compounds — the very great activity and often explosive properties of nitrogen compounds — all these illustrate this fundamental break in properties. We shall see that a somewhat similar break occurs in each case where the atom becomes equally unsymmetrical, namely in the fifth element of each succeeding shell, thus the breaks occur at nitrogen (II*a*), phosphorus (II*b*), vanadium (III*a*), columbium (III*b*), praseodymium (IV*a*).

First Long Period

Beyond argon we soon come into a region where most periodic relations begin to fail. It will therefore be well to examine the present theory rather critically.

With potassium we begin to form a new shell — the third. There are now cells enough to hold 9 electrons in each hemisphere. (Postulate 3.) The first few electrons arrange themselves in much the same way as in the first two periods. Thus potassium, calcium, scandium have properties closely related to those of sodium, magnesium and aluminium. In the first two periods the properties of the atoms just beyond carbon and silicon were electronegative in character because their atoms tended to assume the stable forms corresponding to neon and argon by taking up electrons. But in the third

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period the conditions are quite different. Thus in the atoms of the eighth element of this period, iron, only 4 out of the 9 outside cells in each hemisphere contain electrons. This atom therefore does not have the stability of those of the inert gases and there is thus little tendency for the elements of lower atomic number to take up electrons. The elements titanium, vanadium, chromium, manganese, have therefore predominantly electropositive character. In Table I the differences between the properties of these elements and those of the corresponding elements in the earlier periods is indicated by the heavy lines enclosing these elements. These lines also express the mutual resemblance between the elements.

We can go much further in predicting the properties. The maximum valence of the elements is determined by the ability of their atoms to revert to argon, thus vanadium has a valency of 5, chromium 6, and manganese 7. It will be shown that in the formation of acid radicals with high valences the electrons, although they are given up to oxygen atoms, yet remain within the field of force of the original atom. In other words, the acid-forming atoms share their electrons with oxygen atoms but do not lose them completely. In compounds in which these high valences occur the properties are like those of the corresponding elements of the previous period. Thus vanadates resemble phosphates, chromates resemble sulfates and permanganates are like perchlorates. But when these elements have other valences their properties do not show such relationships.

The electropositive character of potassium, calcium and scandium is determined by the ease with which they revert to argon. Elements like vanadium, chromium and manganese, however, cannot form positive ions by reverting to argon for they would have to give up completely 5, 6 and 7 electrons, respectively. The large electrostatic forces involved prevent the formation of ions with such large charges. The electropositive character of these elements must manifest itself therefore by the formation of ions with fewer charges. The tendency to give up electrons is dependent on the presence of electronegative elements capable of taking up the electrons.[1] In general, we may suppose that the atoms in a metal are held to each other by very strong forces as indicated for example by the high heats of evaporation. If the metal goes into solution a large amount of energy must be expended in separating these atoms and in removing some of their electrons. This energy is supplied by

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[1] The form sometimes given to Nernst's theory by which the tendency to form ions is due to a solution pressure cannot correspond to the true mechanism of ionization. The real tendency of such a substance as potassium to give off electrons is measured by the Richardson work function as determined from the electron emission in high vacuum. The tendency for single atoms of potassium to give off electrons is measured by the ionizing potential. In both cases an energy must be expended to separate electrons from potassium which corresponds to a difference of potential of a couple of volts. I have previously discussed at some length the general theory underlying this statement (Langmuir, *Trans. Am. Electrochem. Soc.* **29**, 125 (1916)).

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the energy of combination of the electronegative elements with the electrons separated from the atoms when they go into solution in the form of ions. Now if a metal forms divalent ions, more energy can be supplied than if it forms univalent ions. On the other hand it will be more difficult to separate two electrons than one electron from an atom. Thus we may suppose in a given case that univalent ions will not form because the energy supplied by the combination of a single electron with the electronegative atom is not sufficient to separate the metal atom from the others. On the other hand quadrivalent ions may not form because the energy necessary to separate 4 electrons from the atom may be greater than that which can be supplied by the combination of the 4 electrons with the electronegative element.[1] It may happen however that both divalent and tervalent ions can form with about equal ease.

As a matter of fact, if we examine Fig. 1 we see that the elements vanadium, chromium, manganese, iron, all form divalent and tervalent cations but form no univalent or quadrivalent ions in solution. The fact that they all form ions of the same valence with so nearly the same ease shows that the stability of these electrons in these atoms is very nearly the same. But this is just what our theory would lead us to expect.

For the elements under consideration only 5 to 8 out of the 18 cells in the third shell are filled with electrons. Furthermore, the tendency of the electrons to line up (Postulate 6) with the underlying electrons of the second shell is gradually being weakened by the mutual electrostatic repulsion. Therefore, the tendencies of these elements to give up electrons do not differ greatly. The lack of definite forces to determine the distribution of the electrons among the cells, renders these elements (according to a theory of Lewis)[2] capable of absorbing light in the visible spectrum. We thus find that they all form colored salts. To quote from Lewis: "The difficulty * * * * lies in the fact that the kernel of these atoms is not uniquely and permanently defined. It seems probable that in these elements there is a possibility of the transfer

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[1] It should be kept in mind that the work which must be done to separate electrons from an atom increases rapidly with the number removed. Thus if 1 represents the work done to remove one electron, the work done to remove the second is 2, the third 3 and the fourth 4. To remove 4 electrons the total work is thus 10 times that needed to remove one. The energy supplied by the formation of the anions increases however in direct proportion to the number of electrons removed. To take a concrete example, let us assume that in terms of the energy units chosen above the formation of each anion supplies 2.7 units, while the separation of the metal atoms from each other requires the expenditure of 2 units per atom. Then the free energy supply and consumption for the differently charged cations are

Number of Electrons	0	1	2	3	4	5
Energy supplied	0	2.7	5.4	8.1	10.8	13.5
Energy consumed	2.0	3.0	5.0	8.0	12.0	17.0

In this case therefore there is sufficient energy to form the divalent or trivalent ion but not sufficient to form the univalent, quadrivalent or quinquivalent ion.

[2] See also Bichowsky, *J. Am. Chem. Soc.* **40**, 500 (1918).

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of electrons either from one part of the kernel to another, or between the kernel and the outer shell, or possibly between two separate outer shells of the same atom and that electrons which are suspended midway between two such stages are responsible for this absorption of light in these cases." According to the present theory the absorption is caused by the transfer of electrons between different parts of the same outside shell or is possibly due to the ease with which an electron is gained or lost by the outside shell. There is no necessity for, and in fact every probability against, the kernel (i.e., the inner shells) being concerned in this process.

In the atoms of iron there are 8 electrons in the third shell, or 4 in each hemisphere. According to Postulate 6 the magnetic forces will make these electrons take positions as close as possible to those of the underlying shell. We may therefore picture the structure of the iron atom as follows: Close to the nucleus are two electrons. The 24 remaining electrons arrange themselves in 3 layers at the corners of 3 concentric cubes (slightly flattened) whose diagonals coincide. Although this atom possesses about as high a degree of symmetry as that of argon it differs radically from the latter in that the outer shell is not saturated, only 4 of the 9 cells in each hemisphere being occupied by electrons (Postulate 3). Furthermore, the number of electrons in the outside shell is beginning to be so great that the electrostatic repulsion (Postulate 6) tends to decrease the stability of this arrangement. These are the fundamental reasons that the elements of smaller atomic number like chromium and manganese do not exhibit the electronegative properties of sulfur and chlorine.

In cobalt and nickel whose atomic numbers are, respectively, one and two units larger than that of iron, the *extra* electrons can no longer be arranged over those in the underlying shell. Let us consider the way that the electrons in nickel arrange themselves. In the outside shell there are 5 electrons in each hemisphere and these tend to arrange themselves over the underlying 4 electrons (II*b*). The only position of reasonable symmetry which the extra electron can take is directly over the center of the square formed by the 4 electrons of the second shell. In other words, the electron goes into the polar axis of the atom. In cobalt there is an electron at one end of the polar axis but not at the other.

The present theory thus explains in a perfectly satisfactory way the anomalous position of iron, cobalt and nickel in the periodic table. We shall see that it also accounts for their unusual magnetic properties.

The ordinary chemical properties of these 3 elements resemble those of chromium and manganese, except that they have lost most of the acid-forming properties because they are so far removed from argon that they cannot revert to it. Thus these 3 elements never show valences of 8, 9, and 10 and do not form acids corresponding to chromates and permanganates. They form predominantly salts in which they exist as divalent or tervalent cations and for the same reasons as those discussed in connection with vanadium,

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chromium and manganese. The colors of their salts are even more marked than those of the chromium and manganese cations which indicates that their electrons are even more loosely bound. With nickel the number of electrons is so great that the electrostatic forces seriously oppose the magnetic forces (Postulate 6). The introduction of the electrons in the polar axis also tends to force the other electrons away from their positions over the underlying electrons and thus still further weakens the magnetic forces. The effect is thus to bring about a rearrangement of the electrons so that the square containing the 4 electrons in each hemisphere, tends to revolve 45° about the polar axis. This arrangement, which we may call the β-form, has a higher degree of symmetry than the α/form previously considered, in that all the electrons in the β-form are as far from the underlying ones as possible, while in the α/form one electron was far from, and the other 4 were close to, the inner ones.

According to Postulate 3 we should look upon the transformation from the α- to the β-form as involving the passage of electrons between different cells in the outside layer. It is perhaps best to imagine that it is the empty cells which arrange themselves over the underlying electrons in the β-form.

The β-form of the nickel atom has a symmetry which exceeds that of any other atom between argon and krypton, with the possible exception of iron. Thus the atoms of the elements above nickel in giving up electrons tend to revert to either nickel or iron. But by the time we get to elements above nickel the large nuclear charge causes the electrostatic forces to predominate over the magnetic so that the tendency to revert to iron is eliminated.

As a matter of fact, by referring to Fig. 1, we find that copper (cuprous) has a valency of 1, zinc has 2, gallium 3, etc., right up to selenium, 6. These elements therefore all tend to give up electrons in such a way that their atoms revert back to the symmetrical β-form of the nickel atom. It must be remembered that after these atoms have given up their extra electrons their outside layers contain the same number of electrons as the nickel atoms but they differ from the latter in that the charge on the nucleus is greater and therefore there is a much greater tendency for the β-form to be the more stable form.

The tendency of the elements above nickel to revert to the β-form of nickel is expressed in Table I by placing Ni β in the same vertical column as the inert gases. The horizontal lines enclosing these elements indicate the distinction between the structure of Ni β and atoms of the inert gases.

In the case of copper we find that the ability to form an ion having an α-form is not wholly lost. Thus copper forms divalent ions. The cupric ions form a continuation of the family of similar elements which extended from vanadium to nickel, but the cuprous salts form a radical departure from this series. The electrons are given up in the formation of cupric ions not because there is any inherent stability in the cobalt atom to which it reverts but for the same

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reason that chromium, manganese, iron, nickel and cobalt form divalent ions. It is interesting to note that the cupric salts are highly colored and in many ways resemble nickel salts. The cuprous salts on the other hand resemble those of no element thus far considered. It is true the atoms have the same valence as those of the alkali metals and that the ions are colorless in both cases showing that all electrons are firmly held. But the solubilities of the salts are very radically different. Now this is just the kind of difference we should expect from the difference between the structure of Ni β and the atoms of the inert gases. The atoms of these gases are characterized by weak secondary valence forces (low boiling points, etc.) whereas atoms having only about half of the cells in the outside shell filled have strong residual fields of force. The properties of the alkali metals are therefore determined almost wholly by the electrostatic charges on their ions, but with ions like that of univalent copper there is in addition the residual field of force due to the large number of unsaturated electrons. The cuprous ion thus tends to form insoluble solid salts and many addition products.

With zinc we have completely broken away from the tendency to variable valence. The salts are now all colorless. The tendency to form molecular compounds (secondary valence) still distinguished this element from the more purely electropositive metal like calcium.

Germanium is interesting since it begins to acquire an electronegative character because of its ability to assume the form of krypton by taking up 4 electrons. It thus resembles carbon and silicon in forming a volatile hydride whereas such a tendency is absent in case of titanium.

In arsenic, selenium, and bromine because of the proximity of krypton, the electronegative character predominates and these elements thus closely resemble phosphorus, sulfur, and chlorine. But their tendency to form insoluble secondary valence products distinguishes them from these other elements.

Magnetic Properties[1]

Before proceeding with the discussion of the elements beyond krypton let us consider the magnetic properties of the elements of the first long period. We have seen that the structures of the atoms of iron, cobalt and nickel differ from those of all the elements so far considered in that there are 24 electrons arranged at the corners of 3 concentric cubes. Furthermore, our theory leads us to believe that they are held in these positions by magnetic forces. It is significant also that Parson[2] was led to assume that the magnetic properties of iron were conditioned by the existence of 4 concentric shells of 8 electrons each

[1] Most of the data used in the following pages have been taken from the excellent review of Theories of Magnetism by S. Dushman (*Gen. Elect. Rev.*, May, August, September, October and December, 1916).

[2] *Smithsonian Inst. Pub.*, Miscel. Collections **65**, No. 11 (1915).

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and that these electrons exerted magnetic forces on each other. Hull[1] in a study of the crystal structure of iron by the X-ray method found that the atoms of iron are arranged according to a centered cubic lattice, that is, each atom is surrounded by 8 others in directions corresponding to the diagonals of a cube. Hull also found that the intensities of the lines in the X-ray spectrum were best accounted for on the assumption "that 8 of the 26 electrons in each atom are arranged along the cube diagonals at a distance from the center equal to one-fourth the distance to the nearest atom. * * * * If all the electrons are displaced from the center of the atom along the cube diagonals in four groups of 2, 8, 8, 8 at distances $^1/_{32}$, $^1/_{16}$, $^1/_8$ and $^1/_4$, respectively, of the distance to the nearest atom, all the observed facts are accounted for within the limit of experimental error." The structure thus proposed by Hull is identical with that to which we are led by our present theory, except that we should expect the radii of the electron shells to be more uniform than the values given by Hull. However this is a point of smaller significance. It is possible that the thermal agitation of the outside electrons which are not under as strong constraints as the others may somewhat modify Hull's results. It should be noted that Hull[2] has found that nickel atoms arrange themselves in a crystal in a similar way to those of iron. He has not, however, determined the probable positions of the electrons.

The ferromagnetic properties of iron, cobalt, and nickel undoubtedly depend not only on the arrangement of the electrons in the atom but also on the arrangement of the atoms with respect to each other. Hull's results indicate that there are 6 electrons in a line between the centers (nuclei) of each pair of adjacent iron atoms. The two which correspond to the outside layer of electrons in the atoms are held by weak constraints, but the inner ones are probably held at least as firmly as those in argon. The fact that the ferromagnetic properties of the metals disappear when these are heated above certain critical temperatures even without change in crystalline form indicates that the outside electrons are subject to thermal agitation which destroys the regular structure necessary for the development of ferromagnetism.

It is suggestive that the next most strongly ferromagnetic substances, besides those considered, are the Heusler alloys which consist of manganese and copper together with smaller amounts of aluminum, arsenic, etc. Copper having too many electrons to give a ferromagnetic metal may supply enough electrons to the manganese atoms to make them take a structure like that of iron. Other elements than copper, such as phosphorus or nitrogen, also give ferromagnetic alloys with manganese. Similarly chromium or vanadium, although to a lesser degree, may form magnetic alloys when combined with other elements. In all these cases it is probable not only that the outer shell of the manganese, chro-

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[1] *Phys. Rev.* **9**, 84 (1917).

[2] *Phys. Rev.* **10**, 691 (1917).

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mium or vanadium atom takes up electrons to revert to iron, but that the atoms arrange themselves in a crystal structure which helps to bring out their magnetic properties (perhaps always the centered cubic lattice).

When iron, cobalt and nickel have been heated above their critical temperatures (756° for iron, 1075° for cobalt, and 340° for nickel) they lose their ferromagnetic properties and become paramagnetic and thus resemble the metals of lower atomic number. The magnetic susceptibility of the elements of the first long period varies in a remarkable manner as the atomic number of the elements increases.[1] Argon is very strongly diamagnetic, potassium is already slightly paramagnetic, and the succeeding elements calcium, titanium, vanadium, chromium and manganese show a very rapid but steady rise in paramagnetism until we come to the strongly ferromagnetic metals iron, cobalt, nickel. Beyond nickel there is a sharp discontinuity for the next element, copper, is slightly diamagnetic. The rest of the elements up to bromine have about the same susceptibility as copper, that is, all are slightly diamagnetic.

The sharp break in the curve between nickel and copper is just what our theory would lead us to expect and it affords striking indication of the correctness of the viewpoint. Still more striking confirmation is to be had in the fact that cupric salts are rather strongly paramagnetic, while cuprous salts are diamagnetic. We have already seen that in the cuprous ion the atom reverts to the β-form of nickel, while in the cupric salts it has properties which correspond closely with those of the divalent ions of iron, cobalt and nickel. In other words, in metallic copper and in cuprous salts the electrostatic forces predominate, as we have already seen, in determining the positions of the electrons while in cupric salts the magnetic forces still play an important part.

It may be asked why argon which contains electrons arranged at the corners of cubes, does not resemble iron in its magnetic properties. According to Langevin's theory of diamagnetism and paramagnetism, the presence of electronic orbits in an atom does not in general cause paramagnetism. If the orbits are so arranged in the atom that they have a resultant magnetic moment equal to zero, then the effect of an increase in the external field is to increase the diameters of some of the orbits and decrease others in such a way that diamagnetism results. It is only when the external field is able to change the direction of the axis of rotation that paramagnetism can occur. In the atoms of the inert gases the electrons (or magnetons since we assume they have a magnetic field of their own) being under very large constraints, arrange themselves so that the magnetic field of the atoms is nearly wholly internal, in other words, so that the magnetic moment is zero. Such atoms are diamagnetic. It is only where the electrons are under much weaker constraints, but yet are held by magnetic rather than by electrostatic forces that we should expect paramagnetism.

[1] A curve giving the susceptibility of all the elements as a function of the atomic number has been published by Harkins & Hall, *J. Am. Chem. Soc.* **38**, 169 (1916).

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Second Long Period

Beyond krypton the second layer in the third shell begins to be filled. The first of the 18 electrons needed to complete this layer (Postulates 3 and 4) arrange themselves with respect to the 8 electrons in the second shell (Postulate 5), just as in the first long period, so that ruthenium has a structure analogous to iron. The 18 electrons in the first layer of the third shell, however, make the symmetry much less perfect than it was in the case of iron. The properties of these elements are more complicated than those of the first long period and there is a greater tendency to form insoluble salts and secondary valence compounds. The elements up to ruthenium are slightly diamagnetic or slightly paramagnetic, but from ruthenium to palladium there is a large increase in susceptibility. This reaches a sharp maximum with palladium and then drops suddenly to a negative value for silver. There is thus the same marked discontinuity as was observed between nickel and copper. But the susceptibility of palladium is only about equal to that of manganese and is thus of quite a different order of magnitude from that of iron, cobalt, or nickel.

According to our theory there can be no doubt but that the extra two electrons in palladium arrange themselves in the polar axis. In the elements beyond this point the electrons around the polar axis seek positions as far as possible from the electrons in the second shell, so that the atoms tend to revert to a β-form of the palladium atom. Thus silver forms colorless univalent ions, cadmium divalent, etc. These properties and their explanation are so nearly like those of the first long period that we need not consider them in more detail.

The "Rare Earth" Period

After xenon the fourth shell begins. There are 32 cells to be filled by electrons before the atom again reaches the stability of an inert gas (niton). The first 3 or 4 elements have predominantly electropositive character and form positive ions whose valency increases by steps of one due to the tendency to revert to xenon. As more electrons are added they will tend, according to Postulate 6, to arrange themselves over the 18 of the underlying third shell, just as in the first long period the electrons arranged themselves over the 8 underlying ones in the second shell. This process yields a series of similar elements having about the same valence, just as we found among the elements from titanium to nickel. By referring to Table I we see that this family of elements corresponds exactly with the rare earth elements. The eighteenth element from xenon is lutecium, and this marks definitely the last of the rare earths.

Since the forces holding these 18 electrons are predominantly magnetic and since the constraints are not of the rigid kind characteristic of the inert gases, we should expect these elements to be paramagnetic. As a matter of fact, the rare earths are the most strongly paramagnetic of any of the elements except those from manganese to nickel. Even barium begins to show a perceptible

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paramagnetism (strontium is diamagnetic). The susceptibilities of only a few of these metals have been determined but the atomic susceptibilities of cerium, praseodymium, neodymium and erbium are, respectively, 2, 7, 11 and 7 times that of manganese. Gadolinium sulfate lies between ferric sulfate and manganese chloride in magnetic properties.

It seems probable that the most marked magnetic properties occur with the elements samarium, europium and gadolinium for these are the eighth, ninth and tenth elements from xenon and thus should correspond most closely in their structure to iron, nickel and cobalt. In samarium there is probably a slight tendency for the 8 electrons in the outside layer to arrange themselves at the corners of a cube, while in gadolinium the two extra electrons are in the polar axis. But in other properties these 3 elements should not differ radically from the other rare earths.

By the time the 18 electrons have been added the electrostatic forces have begun to oppose the magnetic attraction to a marked degree. Therefore, when in tantalum an additional electron is added, the whole outside shell tends to rearrange itself so that the empty cells will come opposite the electrons of the underlying shell. The most symmetrical arrangement of this kind will occur when there are 18 empty cells opposite the 18 underlying electrons. The atomic number of niton in which the fourth shell is complete is 86 — therefore an element having 18 empty spaces in the fourth will have an atomic number 68 corresponding to erbium. The structure of this β-form of erbium has the same kind of stability for large, nuclear charges that we found in the cases of β-nickel and β-palladium. We may therefore expect that the atoms beyond lutecium will show a marked tendency to revert to β-erbium. Thus tantalum with an atomic number 73 tends to lose 5 electrons and tungsten to lose 6. The properties of tantalum and tungsten thus resemble those of columbium and molybdenum, but because of the complexity of the atom to which they revert, and in general because of the large numbers of electrons in their outside shell, their secondary valence forces are more highly developed.

In accordance with the marked change in the electron arrangement beyond lutecium we find that the paramagnetism is practically absent in the elements tantalum and tungsten.

The β-form of the erbium atom contains 18 empty cells arranged over the 18 cells of the third shell. When electrons are added as we pass to elements of large atomic number the first 8 of them naturally tend to arrange themselves at the corners of a cube, because of the magnetic attraction of the 8 electrons in the *second* shell. The next two electrons for reasons of symmetry then arrange themselves in the polar axis. We thus have the 3 "eighth group" elements osmium, iridium and platinum. Because of the weakness of the forces acting between the fourth and the second shell we should not expect strongly developed magnetic properties in these elements. As a matter of fact osmium and iridium have susceptibilities nearly equal to zero, but there is a small but sharp

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rise at platinum making this element about $^1/_4$ as paramagnetic as palladium. The next elements gold, mercury, etc., are distinctly diamagnetic. The same sharp break occurs here as we found between nickel and copper, palladium and silver, lutecium and tantalum, although its magnitude is much less. We may therefore assume that beyond platinum the electrons tend to rearrange themselves in a β-form in which the 10 electrons that have been added since erbium endeavor to get farther away from those of the underlying electrons. The 8 empty cells tend to take symmetrical positions in the atom probably at corners of a cube, and the cells containing electrons, space themselves as best they can. The fact that an arrangement of this kind does not have nearly the symmetry which we found for the β-form of the nickel atom is probably the explanation of the fact that the tendency of the succeeding elements to revert to this β-form of platinum is much less marked than we observed in the cases of reversion to nickel, palladium and erbium. Thus we find that gold and mercury have variable valence differing in this respect from silver and cadmium. Thallium forms univalent and tervalent ions whereas indium forms only tervalent. Lead only exceptionally is quadrivalent, while this seems to be the normal condition of tin compounds. Thus stannous salts are strong reducing agents, but divalent lead salts are not. Bismuth is normally tervalent and forms only a few very unstable compounds in which it is quinquivalent. Antimony on the other hand has about equal tendencies to be tervalent or quinquivalent.

There is an interesting sudden break in the susceptibility curve between lead and bismuth. Gold, mercury and thallium are very slightly diamagnetic, but bismuth is the most strongly diamagnetic element with the exception of the inert gases. In all of the elements between gold and niton the positions of the electrons are determined mainly by electrostatic forces (Postulate 6). But magnetic forces still tend to cause the electrons to arrange themselves in the 8 available cells (at platinum) so that they will be placed as symmetrically as possible with respect to the underlying electrons. Now the 4 additional electrons (in lead) can arrange themselves in the 8 spaces with reasonable symmetry, but the 5 electrons in bismuth cannot do so. The extra electron displaces the others and thus weakens the magnetic forces and strengthens the electrostatic. In agreement with this theory we find that there is a similar, although smaller, minimum in susceptibility at phosphorus, arsenic, and antimony, the elements which also have atomic numbers 3 less than those of the following inert gases. We also find distinct maxima at germanium, tin, and lead which have 4 electrons less than the inert gases which follow them.

The Uranium Period

With niton the first layer of electrons in the fourth shell is completed. As we add more electrons we should expect to go through the same cycle as that of the rare earth period. The properties of the first two or three elements are

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determined primarily by the ease with which they give up electrons. Thus radium very closely resembles barium, differing from it in chemical properties only by its slightly greater secondary valence which manifests itself here by slightly decreased solubility of its salts.

Thorium resembles cerium and zirconium, the elements of similar constitution.

Beyond thorium we might expect another series of elements analogous to the rare earths up to an atomic number of 104 if the nuclei of such elements were stable enough to exist under ordinary conditions. However, the properties of uranium do not bear out this supposition. Uranium is not closely related in its properties to neodymium, nor in fact does it closely resemble any other element. It would seem therefore that it is not safe from our present knowledge to make definite predictions as to the properties of other possible elements of this period.

The Mechanism of Chemical Action and the Structure and Properties of Compounds

The preceding theory of structure of the atoms in the two short periods is nearly the same as that postulated by Lewis. Lewis has discussed how a theory of valence may be derived from this structure. He considers the nature of the single, double and triple bonds, the structure of the ammonium ion, iodine and oxygen molecules, ions such as sulfate perchlorate, etc., the tetrahedral arrangement of the electrons around the nucleus in the carbon atoms, etc. In this way he has fully demonstrated the general value and applicability of the theory. Unfortunately Lewis' treatment of this subject was rather brief and perhaps for this reason it does not seem to have met with the general acceptance which it deserves.

It therefore seems desirable to consider in some detail how this theory may be applied to the predication of the properties of the first 18 elements and their compounds. In doing so we shall considerably extend Lewis' theory and because of the more definite conceptions of atomic structure which we have developed we will be able to apply a somewhat different viewpoint. In particular we shall attempt to explain the "physical" as well as the "chemical" properties of compounds. The predications of these properties depends mainly on Postulates 8, 9, 10 and 11 given below. Following Lewis' practice we will refer to the outside electrons forming an uncompleted shell or layer as "the shell" of the atom, while the whole inner portion, consisting of shells and layers each containing its full quota of electrons, will be called the kernel.

Postulate 8.—The very stable arrangements of electrons corresponding to those of the inert gases are characterized by strong internal but unusually weak external fields of force. The magnetic and electrostatic forces are each very nearly internally balanced. The smaller the atomic number of the element the weaker are these external fields.

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Postulate 9.—The pair of electrons in the helium atom represents the most stable possible arrangement. A stable pair of this kind forms only under the direct influence of positive charges.

The positive charges producing the stable pair may be:

(*a*) The nucleus of any element.

(*b*) Two hydrogen nuclei.

(*c*) A hydrogen nucleus together with the kernel of an atom.

(*d*) Two atomic kernels.

These are listed in the order of their stability.

As we have seen from the previous discussion on atomic structure, the tendency to form a pair of electrons about the nucleus of any atom overpowers the tendency to form other arrangements so that the stable pair constitutes the first shell of all the elements except hydrogen. The tendency for the pair to form around two atomic kernels (Case *d*) is weak and thus only in exceptional cases, under some outside compelling influence does this combination occur.

Postulate 10.—After the very stable pairs (Postulate 9) the next most stable arrangement of electrons is the group of 8 such as forms the outside layer in atoms of neon and argon. We shall call this stable group of 8 electrons the "octet". Any atom up to argon having more than two positive charges on its kernel tends to take up electrons to form an octet. The greater the charge on the kernel the stronger is this tendency. In exceptional cases, the octet can form about a complex kernel, that is, about a structure containing the kernels of two atoms bound together by a pair of electrons (Postulate 9*d*).

Postulate 11, *Electrons Held in Common.*—Two octets may hold 1, 2, or sometimes even 3 pairs of electrons in common. A stable pair and an octet may hold a pair of electrons in common. An octet may share an even number of its electrons with 1, 2, 3, or 4 other octets. No electrons can form parts of more than two octets.

The fact that only an even number of electrons can be held in common probably signifies that the tendency to form stable pairs between the two kernels according to Postulate 9 is a vital factor in the sharing of electrons between octets.

When octets combine together by sharing their electrons fewer electrons are required than if the octets remain separate. Thus when two ocets containing a total of 16 electrons combine so as to hold a pair in common, two electrons are set free. Two octets held together by one, two, or three pairs of electrons thus contain 14, 12, or 10 electrons, respectively. When we consider that the shells of all atoms except those of the inert gases are unsaturated, we see how necessary it is for the atoms to share their electrons with each other if the stable pairs and octet are to be formed.

Lewis discusses two possible arrangements of the electrons in the octet. They may be placed at the 8 corners of a cube or they may be located in pairs at the 4 corners of a regular tetrahedron. In view of Postulates 5 and 11 it would seem that the electrons in the octet are normally arranged in positions corre-

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sponding to the corners of a cube but that the electrons which are held in common between two octets or an octet and a stable pair, are drawn together by magnetic forces to form pairs. Thus we look upon electrons in the atoms as able to move from their normal positions under the influence of magnetic and electrostatic forces. This view does not conflict with that of Postulate 3 according to which the electrons are in cellular spaces. Thus we might assume when there are 8 outside cells that these are in the form of octants of a sphere. In the atom of neon, or the kernel of sodium, or in the chlorine ion the 8 electrons would be arranged nearly at the centers of the octants, but in compounds where pairs of electrons are shared by other atoms, the two electrons forming the pairs are displaced over near the boundaries of the octants and are thus able to come sufficiently close together for the magnetic forces to cause them to form stable pairs.

We are now in a position to apply the theory to explain the properties of the elements and their compounds.

Hydrogen $N = 1$; $E = 1$.[1]—Hydrogen atoms are very active chemically because they tend to combine with any other atoms capable of supplying electrons by which the stable pairs can be formed. We should expect a hydrogen atom to constitute a doublet of high moment which would tend to attract all other bodies. Thus atomic hydrogen is very strongly adsorbed on surfaces.[2] When two hydrogen atoms come in contact their two electrons form a stable pair (Postulate 9*b*) under the influence of the two nuclei so that a molecule, H_2, is produced. This molecule has an unusually weak external field (Postulate 8) and therefore hydrogen has a very low boiling point[3] and is relatively inert chemically except in so far as it can be made to split up into atoms.

Helium $N = 2$; $E = 0$.—In the helium atom the stable pair already exists. Since this is the most stable arrangement of electrons and has the weakest stray field (Postulate 8), helium forms no chemical compounds and has the lowest boiling point and highest ionizing potential of any known substance. Hydrogen has a higher boiling point and lower ionizing potential than helium because the mutual repulsion of the two nuclei forces these apart and increases the strength of the external field.

First Short Period

Lithium $N = 3$; $E = 1$.—Two of the electrons form a stable pair which completes the first shell. The extra electron, just as does that of the hydrogen

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[1] We will use E to denote the number of electrons in the shell of the atom as given in Table I.

[2] Langmuir, *J. Am. Chem. Soc.* **34**, 1310 (1912).

[3] According to the theory which I have advanced (*J. Am. Chem. Soc.* **38**, 2221 (1916); **39**, 1848 (1917)), the so-called physical properties such as boiling point, melting point, surface tension, etc., are manifestations of typical chemical forces, sometimes primary valence, other times secondary valence forces.

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atom, tends to make the atom very active chemically. Lithium atoms are electric doublets and therefore attract one another. There is however now little or no tendency to form stable pairs of electrons (Postulate 9) since the kernels of the lithium atoms are not simple nuclei as were those of hydrogen. Thus after one lithium atom has drawn another one to it there is still just as great a force tending to draw in a third. The electrostatic forces involved are just like those holding together a crystal of sodium chloride. The positively charged lithium kernels and the free electrons will therefore arrange themselves in space in a continuous lattice in a manner quite analogous to that of sodium and chlorine atoms in crystals of sodium chloride. Lithium atoms when allowed to come into contact with each other do not form molecules but form a crystalline solid containing free electrons as part of the lattice structure which is therefore a metallic conductor of electricity. When lithium is melted the structure is not essentially changed except in regard to the regularity of the lattice. The free electrons still occur between the lithium kernels, and the metallic conduction persists. The strong forces exerted by the positively and negatively charged particles on each other makes it difficult to separate the atoms. The great difference between the boiling points of lithium and those of hydrogen and helium is understandable.

When lithium is heated to a sufficiently high temperature, the thermal agitation is able to overcome in some degree even these strong forces so that the lithium evaporates. It is easy to see however that the vapor is monatomic. The energy necessary to separate two atoms of lithium from the surface is about twice that required to separate one, but the kinetic energy of a molecule of two atoms is the same as that of one, so that the momentum is only $\sqrt{2}$ times that of a single atom. Or to look at the problem another way, suppose that a diatomic molecule of lithium, Li_2, does evaporate from the surface, the kinetic energy of agitation of these atoms with respect to each other is the same as when the atoms formed part of the surface. But the forces holding the atoms together in space are in general much less than those which originally held the atoms to the surface. Thus if we assume that the space lattice is like that of sodium chloride each charged particle in the interior has 6 oppositely charged particles around it. A particle in the surface usually has two or three neighboring oppositely charged particles. For these reasons even if some diatomic lithium molecules should leave the surface they would dissociate into atoms at a rate, large compared to that at which they evaporate from the surface. In any case the resultant vapor is monatomic.

The attractive forces between the electrons and the lithium kernels prevent their separation and hence lithium vapor is normally a nonconductor of electricity.

If lithium atoms and hydrogen atoms are brought together the extra electron of the lithium atom and the electron of the hydrogen atom combine together to form a stable pair with the hydrogen nucleus at its center (Postulate 9*a*).

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The lithium kernels thus become lithium ions, Li^+, while the hydrogen nuclei surrounded by the pair of electrons are negatively charged hydrogen ions, H^-. These charged particles would be attracted to each other but since there is no tendency for negative *ions* to form pairs about positive kernels there would be no tendency to form molecules. The lithium and hydrogen ions form a crystalline solid having the composition LiH. Since there are no free electrons, the solid body is a non-conductor of electricity. If melted, however, the positively and negatively charged particles should be able to move under the influence of an electric field so that molten LiH should be an electrolyte (as Lewis has pointed out) in which hydrogen should appear at the anode. The comparative ease with which an electron can be taken from a lithium atom by an electronegative element makes univalent lithium ions stable in water solutions.

The theory thus not only accounts for the chemical activity and valence of hydrogen and lithium as compared to helium, but explains the ordinary properties, such as boiling point, electric conductivity, ionizing potential, etc.

Beryllium $N = 4$; $E = 2$.—The first two electrons form the stable pair, leaving two electrons in the second shell. Since the atom can give up two electrons easily, it forms a divalent ion.

Boron $N = 5$; $E = 3$.—The 3 electrons in the outer shell give this element its tervalent character. The small volume of the atom makes it incapable of forming a tervalent cation. Boron has therefore a more electronegative character than the previously considered elements.

Carbon $N = 6$; $E = 4$; *Nitrogen* $N = 7$; $E = 5$; *Oxygen* $N = 8$; $E = 6$.—We shall consider these 3 elements together because the application of the theory is best illustrated by the compounds they form with each other and with hydrogen. The properties of the atoms up to this point have been determined by their ability to give up one or more electrons. With carbon and the elements which follow it there is less tendency to part with electrons, and more tendency to take up electrons to form a new octet. This opens up new possibilities in the formation of compounds and as a result we find a remarkable contrast between the properties of oxygen and nitrogen and those of lithium and beryllium. The ordinary theory of valence has nowhere been more strikingly useful than in the chemistry of carbon compounds. Among compounds of carbon with hydrogen and oxygen the valence almost without exception can be taken as four for carbon, two for oxygen and one for hydrogen. This simple theory makes it possible to predict with certainty the existence of great numbers of compounds and the non-existence of others.

When nitrogen is introduced into organic compounds there is often much more uncertainty in using this theory of valence. But among the compounds of nitrogen with oxygen the same theory is almost useless. Who, for example, would ever have been able to predict the existence of such compounds as are represented by the formulas N_2O, NO, NO_2, N_2O_4, N_2O_3 and N_2O_5 or HNO, HNO_2, HNO_3, etc., by applying the valence theory that has been so success-

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ful in organic chemistry? But because of its great success in its special field this theory has been nearly universally used even for inorganic compounds. To explain the existence of the above oxides of nitrogen it has thus been assumed that the valence of nitrogen may be one, two, 3, 4 or 5. It is obvious that such a theory must predict the existence of an unlimited number of compounds which do not exist at all. For example, we should have such compounds as are indicated by the formulas NH, NH_2, NH_4, or NCl, NCl_2, NCl_4 and NCl_5.

The degree to which any given theory of atomic structure is able to explain the success of the ordinary valence theory for carbon compounds and its failure for nitrogen compounds should serve as a measure of the value of the theory and should afford information as to whether the theory corresponds to the actual structure of the atoms.

With the exception of compounds like lithium hydride and some compounds of elements having atomic numbers greater than 20, nearly all "primary valence" compounds involve the formation of octets. Let us examine more closely the theory of valence which results from the application of Postulates 9, 10 and 11.

Octet Theory of Valence

Let e be the total number of *available electrons* in the shells of the atoms forming a given molecule. Let n be the number of octets formed by their combination and let p be the number of pairs of electrons held in common by the *octets*. For every pair of electrons held in common there is a saving of 2 p in the number of electrons needed to form the octets. Thus we have

$$e = 8n - 2p. \tag{1}$$

For most purposes it is more convenient to use this equation in the form

$$p = \tfrac{1}{2}(8n - e). \tag{2}$$

When a hydrogen nucleus holds a pair of electrons in common with an octet, this pair should not be counted in determining the value of p, since it does not result in any saving in the numbers of electrons required to form the octets.

To determine e we add together the numbers of available electrons in the outside shells of all the constituent atoms. Thus for every hydrogen we add one, for lithium one, for beryllium 2, for carbon 4, nitrogen 5, and oxygen 6.

Equation 2 gives definite information as to the ways in which the octets in a given molecule can be arranged. This equation applies to all "*octet compounds*", that is, to all compounds whose atoms are held together either because their octets share electrons or because electrons have passed from one atom to another in order to complete the octets.

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Let us now apply Equation 2 to determine the structure of various molecules.

Water (H_2O).—The hydrogen nuclei always tend to hold pairs of electrons, never octets. We thus place $n = 1$, $e = 8$ (6 for the oxygen and one for each hydrogen). Whence, by Equation 2, $p = 0$. This means that no electrons are held in common between octets, which must obviously be the case for any molecule containing only one octet. The fact that we found $p = 0$ thus shows that the compound H_2O can exist. The two hydrogen nuclei attach themselves to two pairs of electrons forming the octet. The arrangement is presumably as illustrated in Fig. 2. The hydrogen nuclei are represented by the + signs and the electrons in the octet by the small circles while the nucleus of the oxygen atom is shown as a black circle. In figures after this one the kernels of the atoms will not be shown.

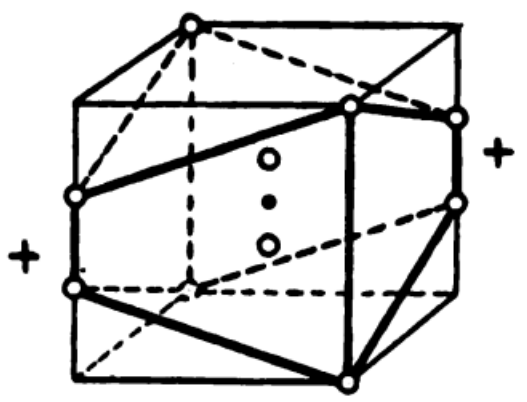

FIG. 2. Diagram of the water molecule.

We see from this structure that water forms molecules which are quite thoroughly saturated. The two hydrogen nuclei are held firmly by the pairs of electrons very much as they are in gaseous hydrogen. All the electrons form an octet and hence (Postulate 8) should have a rather weak stray field of force. Water therefore should be a substance easily volatile as H_2O molecules and should not be a good conductor of electricity in the liquid state. Because of the lack of symmetry of the molecule as compared to the neon atom, water molecules should have a larger external field than neon atoms so that the boiling point should be much higher.

Lithium Oxide, Li_2O.—As before we placed $n = 1$, $e = 8$ and find $p = 0$. The oxygen atoms have completed their octets by taking the two electrons from the two lithium atoms. The lithium kernels however already have their pairs of electrons and therefore cannot form pairs with those of the oxygen octet. Therefore lithium oxide consists of oxygen atoms carrying a double negative charge and of lithium kernels with single positive charge. This substance thus tends to form a solid space lattice structure having low vapor pressure, which is an electrolytic conductor when melted.

Lithium Hydroxide, LiOH, $n = 1$, $e = 8$, $p = 0$.—The hydrogen nuclei are held by a pair of electrons in the oxygen octet but the lithium kernel does not share electron with the oxygen atom. This substance should thus

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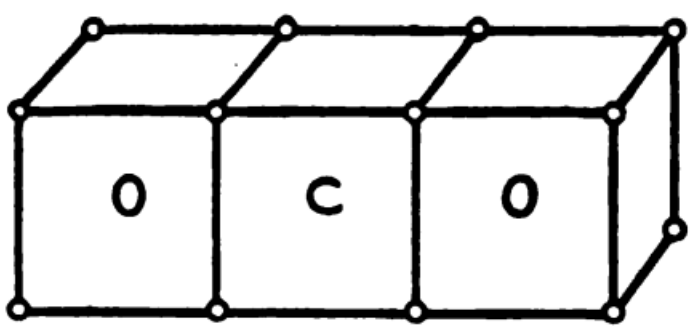
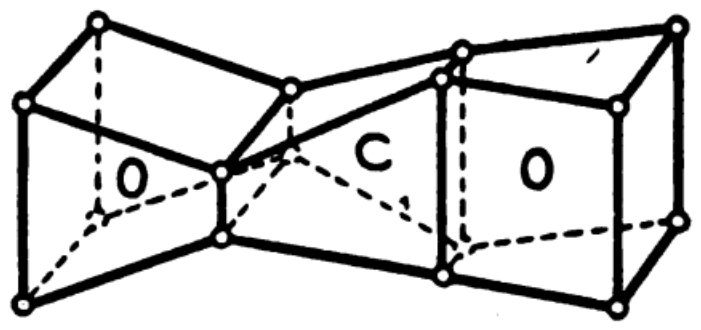
form a solid body showing electrolytic conductivity when molten and capable of dissolving in water as an electrolyte giving ions of Li^+ and OH^-. We should expect lithium hydroxide to be easily soluble in water because the OH^- ion so much resembles water in its structure and the high dielectric constant of water makes it easy for the necessary separation of the positive and negative particles to take place.

Carbon Dioxide, CO_2.—Here each atom forms an octet. We place $n = 3$; $e = 4+2\times6 = 16$, whence, by Equation 2, $p = 4$. Thus 4 pairs of electrons must be held in common by the 3 octets. This leads to a structure like that shown diagrammatically in Fig. 3 or probably better by Fig. 4 in which the pairs of electrons held in common are shown closer together. This places the 4 pairs of electrons forming the octet of the carbon atom at the 4 corners of a regular tetrahedron. The lines connecting the electrons in these figures are used merely to give a better perspective of the arrangement of the electrons and of course should not be taken as representing the boundaries of the atom. In the remainder of the figures no attempt will be made to show the probable closer approach of the electrons forming the pairs, that is, we will use only diagrammatic figures like Fig. 3.





FIGS. 3 and 4. Diagrams of carbon dioxide molecules.

We can readily see that carbon dioxide is a thoroughly saturated non-polar substance which should be a non-conductor of electricity, be very readily volatile and rather inert chemically. The structure of carbon dioxide given by our theory is in full accord with that given by the ordinary valence theory $O = C = O$. By Fig. 3 we see that each pair of electrons held in common is the equivalent of the bond of the ordinary theory. The same was true of the structure found for water. But for lithium oxide and hydroxide there are no electrons held in common; the number of electrons transferred from one atom to the other corresponds to the ordinary valence.

Methane, CH_4.—We place $n = 1$, $e = 8$; hence $p = 0$. The 4 hydrogen atoms supply 4 electrons to complete the octet of the carbon atom. Each hydrogen nucleus is held by one of the 4 pairs of electrons forming the octet. The final arrangement is that the 4 hydrogen atoms are located at the corners of a tetrahedron, each atom held by a stable pair just as it is in the hydrogen molecule. This arrangement is very much more symmetrical than that of the water molecule and should have a much weaker external field.

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Methane should thus be non-polar to an unusual degree; it should be a gas with a fairly low boiling point, and should be a non-conductor even when liquid.

Organic Compounds.—It will be found that Equation 2 leads to results identical with those of the ordinary theory of valence for all organic compounds of carbon, oxygen and hydrogen. In every case each pair of electrons held in common corresponds to a bond. Two and 3 pairs held between two octets correspond to the double and triple bonds respectively.

To show how this theory applies to hydrocarbons let us attempt to find according to the octet theory what substances of the general formula C_xH_y can exist.

From Equation 2, it is evident that in all octet compounds there must be an even number of electrons e, otherwise p, the number of pairs of electrons held in common, would be a fractional number. Therefore in all hydrocarbons there must be an even number of hydrogen atoms since each of these atoms has a single electron. We may therefore confine our attention

TABLE II

	n	e	p	Constitution
CH_2	1	6	1	Impossible
CH_4	1	8	0	CH_4
CH_6	1	10	−1	Impossible
C_2H_2	2	10	3	$HC \equiv CH$
C_2H_4	2	12	2	$H_2C = CH_2$
C_2H_6	2	14	1	$H_3C - CH_3$
C_2H_8	2	16	0	$CH_4 + CH_4$
C_3H_2	3	14	5	Possible only in ring
C_3H_4	3	16	4	$H_2C = C = CH_2$
C_3H_6	3	18	3	$H_3C-C = CH_2$ or as ring
C_3H_8	3	20	2	$H_3C-CH_2-CH_3$
C_3H_{10}	3	22	1	$H_3C-CH_3+CH_4$
C_4H_2	4	18	7	$HC \equiv C-C \equiv CH$
C_4H_4	4	20	6	$H_2C = C = C = CH_2$ or as ring

to hydrocarbons of the general formula C_xH_{2y}. In Table II a series of compounds of this type is analyzed by the octet theory. The first column gives the empirical formula of the hypothetical compound. The values of n, and e are in the next two columns while p calculated by Equation 2 is in the fourth. For CH_2, p is found to be 1. Since a single octet cannot share any electrons with itself it is impossible to form a compound CH_2. In the case of CH_4 we find $p = 0$ which is easily realized since there is only one carbon atom. Therefore the compound CH_4 should exist. The compound CH_6 is obviously impossible since for this the theory gives $p = -1$. For C_2H_2 the equation gives $p = 3$. The carbon atoms must therefore have 3 pairs of electrons in common. If we represent each pair by the line used to indicate a valence bond, the carbon atoms are represented by $C \equiv C$. There is no question

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as to where the hydrogen atoms must go. It is impossible to have $C \equiv CH_2$ because such a structure would require *five* pairs of electrons around one carbon atom. The formula therefore must be $HC \equiv CH$. In a similar manner we arrive at each of the other formulas. The only cases where the pairs of electrons can be shared between the octets of the carbon atoms in more than one way are the cases where isomers should exist according to the ordinary valence theory. Once having decided where the pairs of electrons are located, there is never any possibility of arranging the hydrogen atoms in any other than one way. The theory applies exactly as well to ring compounds as to chains.

The Equation 2 is thus a complete mathematical statement of the valence laws for hydrocarbons.

For carbon-oxygen-hydrogen compounds the theory works out in about the same way. All the structures given by the ordinary theory can be found by the octet theory and in every case each bond corresponds to a pair of electrons. An illustration of a compound of this type will help to make this clear.

Acetic Acid, $C_2H_4O_2$.—Here $n = 4$, $e = 2\times4+4+2\times6 = 24$; whence $p = 4$. The 4 pairs of electrons may be distributed in several ways such as $C=C\begin{matrix}O\\O\end{matrix}$, $C-O-C=O$, $C-C\begin{matrix}=O\\O\end{matrix}$, etc.[1] These correspond to the compounds $H_2C=C\begin{matrix}OH\\OH\end{matrix}$, $H_3C-O-CH=O$ and $H_3C-C\begin{matrix}=O\\OH\end{matrix}$ the last one being acetic acid.

Thus if we apply the octet theory to a compound $C_2H_4O_2$ we find the same isomers that we would be led to by the ordinary valence theory. The ordinary valence theory sometimes indicates the possibility of compounds which we have never been able to prepare as for instance $C(OH)_4$. For organic compounds the octet theory will be no better than the ordinary valence theory in this respect — the results will always be indentical. But we shall see that this identity disappears in the case of inorganic compounds.

Oxides of Nitrogen.—There is hardly a case where the ordinary valence theory fails so completely as when it is applied to the oxides of nitrogen. Let us try to deduce from the octet theory what oxides of nitrogen might be capable of existence and what the structure of their molecules must be.

---

[1] As far as the application of Equation 2 is concerned we might also arrange the pairs of electrons thus: $O-C=O-C$ corresponding to a compound, $O-CH=O-CH_3$. It is only by taking into account the fact, to be discussed later, that oxygen has a tendency to share either one or two pairs of electrons and only rarely shares 3 pairs, that we can predict that a compound of the above type does not exist. With sulfur, compounds of this general type frequently do exist.

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In the first place from Equation 2 we see that the total number of available electrons in the molecule must be even. Since nitrogen has 5 electrons in its shell and oxygen has 6, there will always be an odd number of electrons, unless the number of nitrogen atoms is even. We will therefore apply our theory to investigate the structure of the series of oxides represented by N_2O_x as given in Table III.

TABLE III

Structure of Nitrogen Oxides

		n	*e*	*p*	Structural formulas
1	N_2O	3	16	4	N = O = N, or N = N = O
2	N_2O_2	4	22	5	O = N−N = O
3	N_2O_3	5	28	6	O = N−O−N = O, or O = N(O)−N = O
4	N_2O_4	6	34	7	O = N(O)−N = O
5	N_2O_5	7	40	8	O = N−O−N = O
6	N_2O_6	8	46	9	Impossible
7	N_2O_7	9	52	10	Impossible

The values of p calculated from Equation 2 are given in the fifth column. The most probable structural formulas based on these values of p are given in the last column. In these formulas, as throughout the rest of this paper, each dash represents a pair of electrons held in common between adjacent atoms, just as in the formulas of organic compounds.

When $x = 1$ we find that our theory indicates that such a compound has the formula N = O = N or N = N = O. Because of its simplicity and symmetry we should expect such a compound to exist. The actual arrangement of the electrons is shown diagrammatically in Fig. 5.[1] According to the octet theory there is no difficulty at all in explaining the existence and properties of this substance. Its structure is exactly like that of carbon dioxide (Fig. 3). We should thus expect it to be a gas having about the same boiling point as carbon dioxide. Its oxidizing properties at high temperatures are due to its decomposition into oxygen and nitrogen which is made an irreversible process by the great and unusual stability of the nitrogen molecule.

Let us proceed with the oxides of nitrogen. When $x = 2$ (Table III) we find that a possible arrangement is O = N−N = O. This formula is identical to that which we obtain by the ordinary theory if nitrogen is taken as tervalent. The fact that this compound does not exist as a gas, but presum-

[1] There is good evidence that nitrous oxide has the structure N = N = O rather than that shown in Fig. 5. The arrangement of the electrons however remains the same.

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ably dissociates into NO is not explained by the octet theory but neither is it by the ordinary theory.

According to the octet theory N_2O_3 may have at least 3 different structures $O=N-O-N=O$, $O-N=O=N-O$ or $O=\overset{O}{N}-N=O$ whereas by the ordinary theory with tervalent nitrogen — only the first should be possible. In view of the ease with which N_2O_3 breaks down to NO and NO_2 and by comparison with the formula for N_2O_2 which breaks down into NO it seems that the third of the above formulas is the most probable structure.

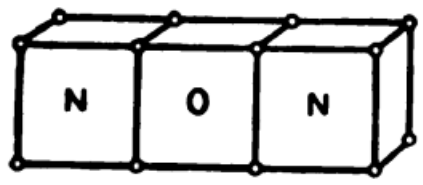

Fig. 5.

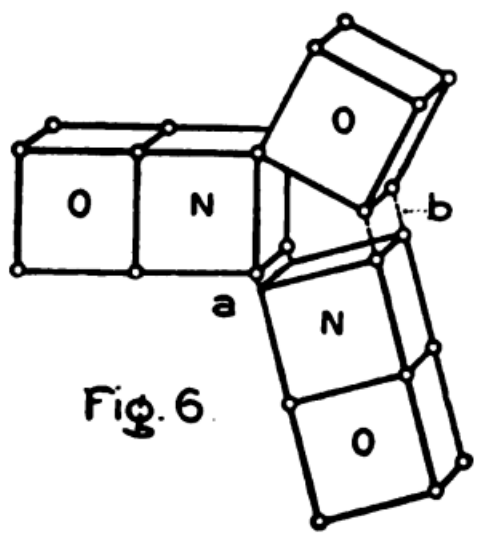

Fig. 6.

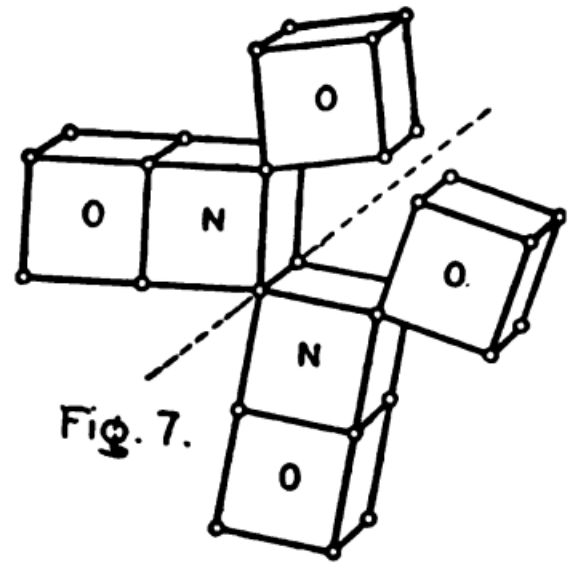

Fig. 7.

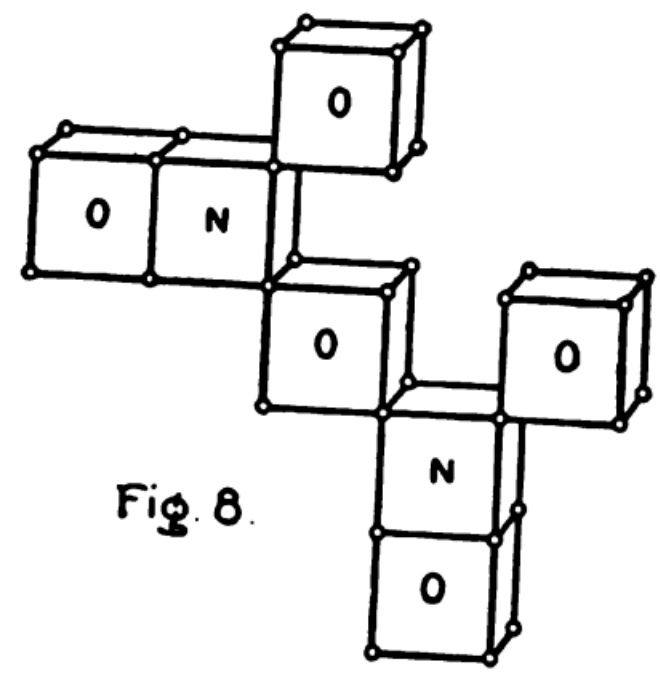

Fig. 8.

FIGS. 5, 6, 7 and 8. Diagrams of molecules of the oxides of nitrogen.

The deep blue color of liquid N_2O_3 indicates the presence of very loosely held electrons. This suggests tautomerism between the first and third forms as shown in Fig. 6. If a pair of electrons is held in common at *a* we have the third formula while if it is held at *b* the structure is as given by the first formula. This tautomerism involves the shifting of two electrons between the positions *a* and *b*.

The structure of N_2O_4 derived by the octet theory as given in Table III is as shown in Fig. 7. By comparing this with Fig. 6 we see that the extra oxygen atom has made the molecule incapable of tautomerism like that between the two forms of N_2O_3. On the other hand, the molecule still tends

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to dissociate into two parts (NO_2) as shown by the dotted line. The stability of the electrons in N_2O_4 causes this to be a colorless compound.

The octet theory also explains the existence of N_2O_5 and leads to the structure shown in Fig. 8. There are no unstable electrons so this compound is colorless. It tends to decompose as indicated by dotted lines into NO_2 and oxygen, although not nearly as readily as does N_2O_4.

When we apply the octet theory to the case that $x = 6$, or 7 we find (see Table III) that the value of p becomes so large that there are not enough electrons in the atoms to form the pairs, except by forming chains of oxygen atoms or a ring structure. Even on the ordinary theory we could account for any numbers of oxygen atoms if we could string them out in chains thus as for example $O = N-O-O-N = O$. We see that such a structure as

$$\begin{matrix} \ \ O\ \ O \\ ONONO \\ \ \ O\ \ O \end{matrix}$$

is impossible, since by Table III we would have $p = 10$ and this would require more electrons in the shell of the nitrogen atom than there actually are. The octet theory thus explains without difficulty the existence and properties of N_2O, N_2O_3, N_2O_4 and N_2O_5, although the ordinary theory fails to do so. Both theories fail to explain the existence of NO and NO_2. We shall see however that these compounds may be explained by a modification of the octet theory which we shall consider later.

Nitrogen Acids.—The structures of the three acids HNO, HNO_2 and HNO_3 are given by the octet theory without the necessity of assuming variable valence. Thus for HNO, $n = 2$, $e = 12$ and $p = 2$. This gives a structure represented by $HN = O$ or $HO = N$ and shown in Fig. 9. In a similar way we obtain the structures for HNO_2 and HNO_3 as given in Fig. 9. It should be noted that the group $O = \overset{|}{N} - O$ which occurs in HNO_3 is the same as in the formulas for N_2O_3, N_2O_4 and N_2O_5. The group $O = N-O-$ in HNO_2 was previously found in the *b*-form of N_2O_3 shown in Fig. 6. We see that although HNO, HNO_2, HNO_3 can exist, HNO_4 cannot exist, for in this last case $p = 5$ which would require 10 electrons around the nitrogen kernel.

Nitrogen-Hydrogen Compounds.—The octet theory indicates that NH_3, and H_2N-NH_2 should exist and have the properties they do. The compounds NH, NH_2, NH_4 and NH_5 cannot exist since in these cases we find $p = 1$, $\frac{1}{2}$, $-\frac{1}{2}$, and -1 respectively, whereas p must be equal to zero for a single octet. The theory thus automatically shows the radical difference between the number of oxygen and hydrogen compounds that may be formed. For the ammonium ion, NH_4, we find $n = 1$, $e = 8$ and $p = 0$. The structure of this ion is thus exactly like that of the methane molecule. The positive charge is the cause of its resemblance to the potassium ion.

Hydronitric acid, NH_3, gives $n = 3$; $e = 16$, and therefore $p = 4$. This leads to the formula $HN = N = N$ as the most probable structure.

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Peroxides.—In the oxides of nitrogen and in the nitrogen acids we have seen how oxygen atoms can attach themselves to any octet in which two or more of the electrons are not already held as stable pairs. Thus in Fig. 9, HNO_3 is obtained merely by adding an oxygen atom to the only remaining free pair of electrons belonging to the nitrogen atom of HNO_2. Since oxygen atoms have 6 electrons, they can form an octet by sharing two electrons with some atom which already has an octet. In the case of the nitrogen acids this process could go on until all of the electrons of the nitrogen octet were shared

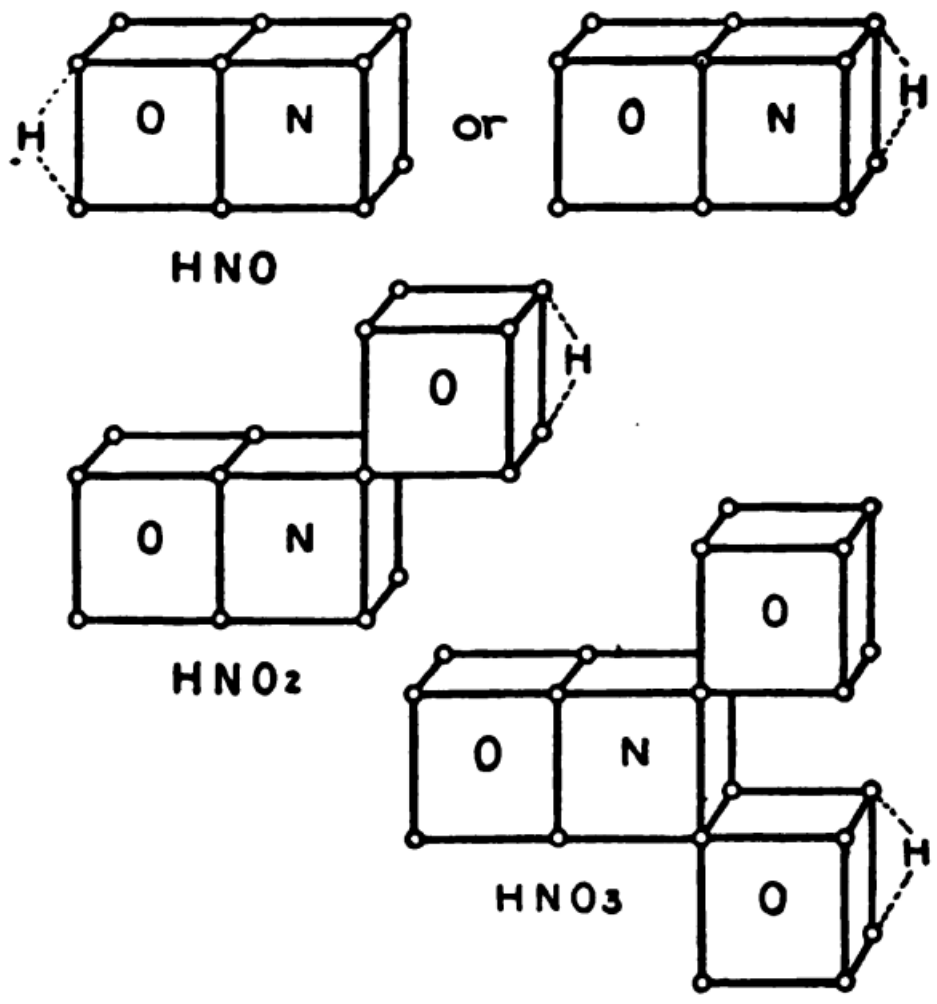

FIG. 9. Diagrams of molecules of nitrogen oxy-acids.

with oxygen atoms. This is quite analogous to the addition in organic molecules, of CH_2 groups which also have 6 available electrons.

We shall see that oxygen atoms can thus add themselves not only to nitrogen atoms but to chlorine, bromine, iodine, phosphorus, sulfur, and other atoms. They can also add themselves to some extent to each other. Thus if we apply the octet theory to hydrogen peroxide, we find $p = 1$. This leads either to the structure HO—OH, or equally well to the structure H_2O—O as shown in Fig. 10.

As a matter of fact, the hydrogen nuclei are probably very mobile and readily shift from one pair of electrons in an octet to another. It may well be that the ease with which this shift occurs is the cause of the high dielectric constant of such substances as H_2O, NH_3, etc. Such an effect does not exist in the case of the hydrogen in hydrocarbons, for all the electrons in the carbon octets are held as stable pairs so that the hydrogen atoms cannot shift positions. The structure given in Fig. 10*b* for H_2O_2 agrees well with

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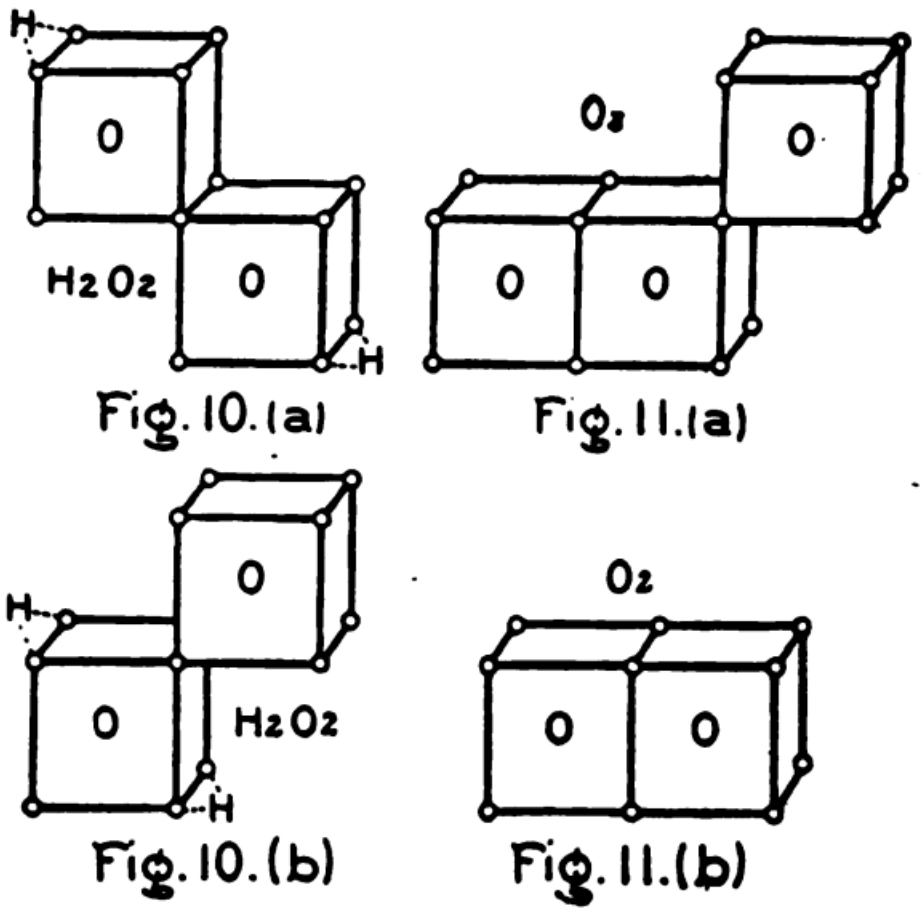
most of its properties. According to the ordinary theory this structure implies a quadrivalent oxygen atom. But the octet theory requires nothing at all unusual in the properties of the oxygen atom.

In a similar way for ozone we find $p = 3$ which leads to the formula O = O—O as shown in Fig. 11*a*. For the oxygen molecule, however, we find $p = 2$ so the structure is O = O as shown in Fig. 11*b*. This structure for



FIGS. 10(a), 10(b) and 11(a), 11(b). Diagrams of molecules of hydrogen peroxide and ozone.

ozone brings out its relationship to the peroxides much better than the ring structure suggested by the ordinary valence theory. The structure and symmetry of the oxygen molecule account for its stability and the low boiling point of liquid oxygen.

The Structure of the Nitrogen Molecule.—The properties of elementary nitrogen are in many ways extraordinary. The contrast between the properties of carbon and nitrogen, elements adjacent to each other in the Periodic Table, could hardly be more striking. Carbon does not melt even at 3700°C while nitrogen has a lower boiling point than any substance except hydrogen, helium and neon. Nitrogen, although many compounds with oxygen exist, combines with oxygen only at exceedingly high temperatures and even then only to a small degree. Carbon, notwithstanding the great affinity of its atoms for each other as shown by its low vapor pressure, combines readily with oxygen at moderate temperatures. Even at the temperature of melting tungsten (about 3600°K) there is evidence that nitrogen is not appreciably dissociated into atoms.[1] This stability of the nitrogen molecule, which is so much greater than

[1] Langmuir, *J. Am. Chem. Soc.* **34**, 876 (1912).

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that of a compound such as carbon dioxide, must be due to some unusual kind of structure.

If we apply the octet theory to the nitrogen molecule by placing $n = 2$; $e = 10$ we find $p = 3$. We are thus led to the formula N ≡ N for the nitrogen molecule. Now in acetylene we have an illustration of two atoms holding 3 pairs of electrons in common. Such a substance is endothermic, forms addition products easily, and even by itself is relatively unstable. A structure of this kind could not possibly account for the properties of nitrogen.

In its boiling point and in fact in most of its properties elementary nitrogen resembles argon. The boiling points of gases on the absolute scale, being approximately proportional to the molecular heats of evaporation, serve as a measure of the external field of force of the molecules. By examination of a large number of organic compounds it appears that the freezing point is dependent to a marked degree on the symmetry of the molecule — the more symmetrical the molecule, the higher is the freezing point. The following table gives the freezing points and boiling points of oxygen, nitrogen and argon on the absolute scale:

	O_2	N_2	Ar
Freezing Pt	38°K	63°	85°
Boiling Pt	90°	77°	87°
Difference	52°	14°	2°

Judging from these boiling points the nitrogen molecule must have a weaker external field of force than either that of oxygen or argon. The differences between the freezing points and boiling points indicate that the nitrogen molecule is very much more symmetrical than that of oxygen and approaches that of argon. The outside layer of electrons in the argon atom consists of a single octet. The evidence given above suggests that the nitrogen molecule also has an outer shell consisting of a single octet. Is such an arrangement possible?

The two nitrogen atoms in a molecule have a total of 14 electrons. We may assume that each nucleus binds two electrons to form a stable pair according to Postulate 9. The two nitrogen kernels, each with 5 positive charges, are then surrounded by a total of 10 electrons. There are thus two electrons more than are needed to form the octet. In view of the stability of the octet (Postulate 10) and the relatively large charges on the two kernels, it seems reasonable that the pair of extra electrons should be imprisoned within the octet and be held by the two nitrogen kernels (Postulate 9*d*) as shown in Fig. 12.

Structures of this kind are not usual but it is evident that in this case there are a number of exceptional factors operating to bring about just this result. The original nitrogen atoms are thoroughly unsaturated and very unsymmetrical and thus have large external fields of force. The number

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of electrons (5) in each shell is such that two atoms cannot form a molecule by forming two octets unless 3 pairs are held in common, something which seldom occurs with nitrogen atoms. Three nitrogen atoms cannot combine to form a single molecule, for this would give an odd number of electrons. Finally, it so happens that there are only two electrons too many to form a complete single octet, and that there are two kernels of small volume but with large positive charges, to bind this extra pair.

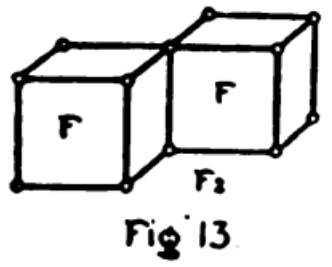

Fig 13

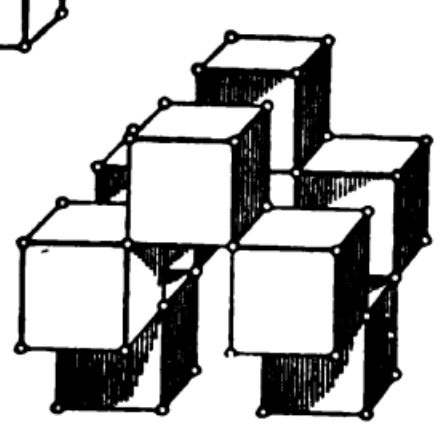

Fig 17

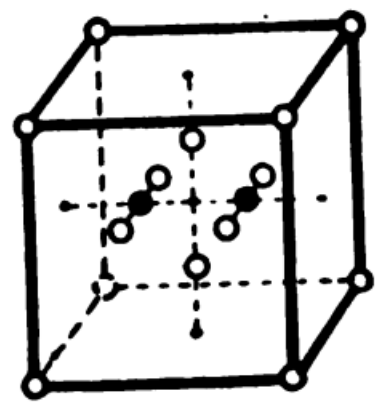

Fig. 12.

FIG. 12. — Diagram of the nitrogen molecule.
FIG. 13. — Diagram of the fluorine molecule.
FIG. 17. — Diagram of the sulfur molecule S_8.

This structure of the nitrogen molecule explains in a perfectly satisfactory way all the remarkable properties of elementary nitrogen previously mentioned. The high heat of formation of nitrogen molecules from the atoms accounts for the great number of endothermic and explosive nitrogen compounds. It is also evident why elementary nitrogen is so unusually inert, while in its compounds it is one of the most active of the elements.

Carbon Monoxide.—The structure of the molecule of this gas has long been a puzzling problem. According to the ordinary valence theory, carbon in this compound must be divalent, and hence should be very much unsaturated. Yet carbon monoxide is a relatively inert substance. Its very low boiling point proves that its molecules have very little external field of force. Its small solubility in water, and the difficulty of finding chemical substances which combine with it at room temperature, do not fit in well with the theory of the divalent carbon atom, for such an atom should show much more active properties — logically its properties should resemble those of atomic hydrogen.

As a matter of fact carbon monoxide resembles nitrogen to an extraordinary degree, as shown by Table IV, which indicates that the physical properties of these two gases are identical almost within the probable limits of experimental error.

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TABLE IV

Physical Properties of Gases

	CO	N_2	Ar	O_2	NO
Freezing point, degrees K	66	63	85	38	106
Boiling point, degrees K	83	78	87	90	120
Critical temp., degrees K	122	127	156	155	180
Critical pressure, atm	35	33	53	50	71
Critical volume	5.05	5.17	4.04	4.26	3.5
Solubility in water, O°C (%).	3.5	2.4	5.8	4.9	7.4
Density of liquid at boiling point . .	0.793	0.796	....	....	...
Viscosity, $\eta \times 10^6$ at 0°C	163	166	210	187	165

This evidence alone should be sufficient to prove that the structure of the shell of the carbon monoxide and the nitrogen molecule must be nearly identical.

However, the case is still stronger when we consider that the total number of electrons in the molecules is the same in both gases. Thus in one case we have two nitrogen atoms with 7 electrons each, while in the other we have carbon with 6 and oxygen with 8. Evidently the reasons which led us to assume that the nitrogen molecule has an outside shell, consisting of a single octet apply with the same force to the carbon monoxide molecule.

In the carbon monoxide molecule there is then an imprisoned pair of electrons within the octet held as a stable pair by the carbon and the oxygen kernels having charges of 4 and 6, respectively.

This theory explains why nitrogen and carbon monoxide are alike in all properties in which a separation of the kernels is not involved. The fact that the two kernels have unequal charges makes it much easier for this structure to break down. Thus while nitrogen shows no signs of dissociating at temperatures of a couple of thousands of degrees, carbon monoxide enters into a few reactions even at room temperature and many reactions at temperatures of a few hundred degrees. Its reaction velocity is however usually very slow indicating that only a small fraction of the molecules is in a form in which the kernels can be separated.

Once the kernels have been separated the carbon monoxide behaves like a very much unsaturated body. It seems probable that at higher temperatures, the carbon monoxide exists in two tautomeric forms — one in which the outer shell is a single octet, and the second in which there are two octets. According to the octet theory the formula of this second form would be $C \equiv O$. This would immediately react with oxygen atoms to form $O = C = O$.

Nitric Oxide.—Lewis has pointed out that among the first 20 elements there are only about a half dozen cases in which there is an odd number of electrons in a molecule. With the exception of nitric oxide, these are all substances which by their color or their intense chemical activity act as though they might have a free electron either in the outside shell or close to it.

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Nitric oxide however is colorless and very stable even at high temperatures. Although it reacts with oxygen to form nitrogen dioxide, this reaction takes place rather slowly, so that the claim can hardly be made that the substance has remarkable chemical activity. Compared to the other oxides of nitrogen it is characterized by its very low boiling point.

The molecule of this substance contains 15 electrons — just one more than the molecules of nitrogen or carbon monoxide. It seems most probable that it has a similar structure and that the extra electron is imprisoned within the octet comprising the shell. This process seems more probable when we remember that the two kernels of the nitric oxide molecule have a total of 11 positive charges as compared to the 10 in the nitrogen and carbon monoxide molecule. With this structure the odd electron is so placed that it does not produce the effects usually characteristic of an odd electron. It is of interest in this connection that nitric oxide is remarkably paramagnetic. This is undoubtedly dependent in some way on this internal odd electron.

According to the last column of Table IV the properties of nitric oxide differ very appreciably from those of nitrogen and carbon monoxide, but not more so than we should expect from the presence of an extra electron within the shell. All the differences in properties shown in this table indicate that the odd electron increases the external field of the atom. The greater chemical activity as compared to nitrogen and carbon monoxide is also due to the same cause.

Hydrocyanic Acid.—There has been much discussion as to the constitution of this compound. It is generally agreed, I think, at present that it has a divalent carbon atom like that in carbon monoxide and is represented by the formula H—N = C.

The total number of electrons in this molecule is 14 — the same as in the nitrogen and carbon monoxide molecules. This fact together with its resemblances to carbon monoxide suggest that here again we have an imprisoned pair of electrons within an outside shell consisting of an octet. The total charges on the kernels of nitrogen and carbon is 9 instead of 10 as in the nitrogen and carbon monoxide molecules. This somewhat decreases the stability and at the same time gives a negative charge to the CN radical so that it must combine with a hydrogen nucleus, or form a negative ion. Two such ions can combine by sharing a pair of electrons — thus releasing the electrons and leaving the uncharged cyanogen molecule $(CN)_2$. It is well known that cyanogen has a very close resemblance to chlorine in many ways. Thus chlorides and cyanides are often isomorphous; silver chloride and cyanide have similar solubilities, etc. The theory of the constitution given above indicates that this resemblance is not accidental, nor is it merely due to the fact that both ions are univalent. It depends on the fact that both the cyanogen ion and the chlorine ion have outside shells that consist of a single octet. The relation between these two ions is like that between elementary nitrogen and argon.

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It seems that these 4 substances, nitrogen, carbon monoxide, nitric oxide and cyanogen, are the only ones in which this double kernel within a single octet is possible. That this is so is also suggested by the symmetrical way in which carbon monoxide, nitric oxide, and cyanogen are related to nitrogen, the element which lies just between C and O in the periodic table. With the exception of these four substances having a special structure and such an obviously unsaturated compound as nitrogen dioxide we have found that all the ordinary compounds of carbon, hydrogen, nitrogen and oxygen fit in well with the simple octet theory. This theory accomplished exactly what we stated the ideal theory of atomic structure should do — namely, it leads automatically to a valence theory for carbon-hydrogen-oxygen compounds which is identical with that in common use, while at the same time it indicates that this ordinary valence theory is inapplicable to nitrogen-oxygen compounds. The octet theory on the other hand applies equally well to nitrogen-oxygen compounds as to organic compounds. In all cases it leads to more definite conceptions of the structure of molecules and compounds and explains their chemical and so-called physical properties very much more completely than the older valence theory was ever able to do.

Let us now continue with a consideration of the properties of the elements and their compounds.

Fluorine $N = 9$, $E = 7$.—The fluorine atom has 7 electrons in its shell. Its properties are therefore largely determined by the tendency to take up an additional electron to complete the octet. In the elementary state two atoms combine together to form a molecule because by so doing each atom can complete its octet. Thus if the molecule is F_2 we have $n = 2$; $e = 14$, whence $p = 1$. By sharing a single pair as shown in Fig. 13, both octets are completed.

The very low boiling point of fluorine indicates that the stray field around this molecule is small. On the other hand the remarkable chemical activity shows that there is a strong tendency for these atoms to avoid sharing their electrons with each other. Thus when lithium and fluorine are brought together, the extra electrons from the lithium atoms are taken up by the fluorine atoms and thus each atom is able to get its own octet instead of being compelled to share it with another atom. The very large heat of formation of lithium fluoride (about 110,000 calories per gram molecule) must be, in greater part, the heat equivalent to the difference between a free octet and one which shares two of its electrons. The energy liberated when an *atom* of fluorine, with its 7 electrons in the shell, takes up another electron would be greater than the above by the energy required to dissociate fluorine into atoms — a quantity which has never been determined but which must be very large.

The question arises, why do atoms share their electrons with each other, if there is such a tendency for the octets to stay separate. The answer, of course, is that there are not enough electrons in the outside shells of atoms to form octets around their kernels unless they share them with each other. Furthermore

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most atoms if they completed their octets, without sharing electrons would have very high charges on their atoms which would tend to prevent their formation.

Hydrofluoric Acid, HF. — The electrons from the hydrogen allow the fluorine atoms to have separate octets. The hydrogen nucleus is then held by a pair of the electrons forming the octet. The large heat of formation of hydrogen fluoride (38,000 calories) notwithstanding the fact that hydrogen atoms have to dissociate during the process, indicates that with fluorine there is little tendency to avoid sharing one of the pairs of the octet with a hydrogen nucleus. This is another illustration of the fact brought out in Postulate 9 that the tendency to form a stable pair between a kernel and a hydrogen nucleus (Case *c*) is much greater than the tendency to form a pair between two kernels (Case *d*).

The molecule of hydrogen fluoride from its structure should have a small stray field. Most of its surface is like that of a neon atom and the part where the hydrogen nucleus is resembles that of a hydrogen molecule. However, the lack of symmetry should increase the stray field much above that of either neon or hydrogen. We should thus expect HF to be a gas or liquid not greatly different from water in its boiling point. As a liquid it should be a non-conductor, but because of its polar character, it forms an electrolyte when dissolved in water. That it forms a rather weak acid in water solution is, I think, due to the small volume of the fluorine atom which greatly increases the electric force tending to prevent dissociation. The whole question of the effect of atomic volumes on the properties of the atoms will be discussed in another place.

Lithium Fluoride, LiF.—This consists of positively charged lithium kernels and negatively charged fluorine atoms. It is therefore a solid salt, which conducts electrolytically when molten.

Carbon Tetrafluoride, CF_4.—By applying the octet theory taking $n = 5$, $e = 32$, and we find $p = 4$. Or we can take $n = 4$ and get $p = 0$. In the first case the carbon atom shares its electrons with 4 fluorine atoms, while in the second it gives up 4 electrons to the fluorine atoms, these fluorine ions being then held by electrostatic forces to the positively charged carbon kernel. In general the first structure would be much more probable but in view of the exceptional properties of fluorine and the difficulty with which it shares electrons it may well be that the second structure applies to this case.

Nitrogen or oxygen alone does not form any compounds with fluorine. Together they form NO_2F and NOF, both gases resembling fluorine in their chemical activity. This fact is very interesting, for NO_2 and NO are remarkable in that they both exist separately but *have an odd number of electrons*. The fluorine atom, which has an abnormally large affinity for an electron, takes the odd electron from these substances even though it is incapable of combining with oxygen or nitrogen in any other form.

The reasons that fluorine does not form compounds with nitrogen, oxygen or chlorine seem to be as follows:

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Helium and neon have the most stable atoms of any of the elements. More energy must be expended to remove an electron from these atoms than from any of the others. The elements hydrogen and fluorine which differ from helium and neon in having one electron less should be expected to have the strongest tendencies to take up electrons. However, this argument needs a radical modification in the case of the hydrogen atom for the charge on this nucleus is only half that on the helium nucleus. The tendency for the hydrogen atom to take up an electron will therefore be very much less than that of the helium atom to hold its electrons. In the case of fluorine and neon this effect is not so serious for the charge on the fluorine kernel is $^7/_8$ of that on the neon kernel.

There is another factor, moreover, which largely eliminates the electronegative character of hydrogen, namely, that the stable pair of electrons held by the hydrogen nucleus can at the same time form part of an octet. For example, consider what must happen if we bring together a hydrogen atom and a fluorine atom. Let us suppose for a moment that the hydrogen atom has such a great affinity for an electron that it takes an electron from the fluorine, leaving this with only 6 electrons. The positively charged fluorine then attracts the negatively charged hydrogen, and, since the stable pair can at the same time form part of an octet, the fluorine is then able to bind the hydrogen nucleus together with its pair. For this reason the tendency of the hydrogen nucleus to take up electrons does not interfere with other electronegative elements getting theirs. Hydrogen therefore can hardly be classed as an electronegative element.

According to our theory therefore fluorine should be the most strongly electronegative element, while for similar reasons chlorine and oxygen should come next.

Fluorine in the free state, F_2, already has enough electrons to form an octet about each atom. The atoms however strive to get a structure exactly like that of neon, that is, one in which each atom has 8 electrons of its own. This means that fluorine has comparatively little tendency to combine with other elements except insofar as it can acquire its electrons outright. That is, it has a strong tendency to *take electrons from* other atoms instead of sharing them with other atoms. Now oxygen, nitrogen, and chlorine, as elements as well as in their compounds, always have octets around their kernels. The fluorine molecule therefore in order to take electrons from these electronegative elements must break down these stable octets. Undoubtedly atomic fluorine would be able to do so, but it is natural enough that molecular fluorine which already has an octet for each atom (although shared) should not be able to accomplish this. On the other hand elements like boron, silicon, phosphorus, and sulfur form some compounds in which their atoms do not contain octets, but hold the surrounding atoms by means of their charge. The charge on the kernels of these elements is not so great but that fluorine can take their electrons. It is true that the fluorine compounds of carbon and silicon and a few compounds with other elements do seem to involve a sharing of electrons between the fluo-

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rine atom and that of the other element, but it is probable that it is easier to share electrons with atoms having small charges on their kernels than with those having large charges.

The fact that fluorine prefers to share electrons with its own atoms rather than with those of any except more electropositive elements such as carbon, phosphorus, etc., is probably due mainly to the greater symmetry of the molecule formed in this way.

Neon.—The atoms of this element already having complete and separate octets have no tendency to take up or give up electrons nor to share them with other atoms. Neon thus forms no primary valence compounds. However there is a stray field of force around the atoms and this accounts for the liquefaction and solidification of the gas at low temperatures.

Second Short Period

The atoms of the elements beyond neon easily give up electrons and revert to the form of neon. The first two elements, sodium and magnesium, have properties which are practically wholly dependent on this giving up of electrons. With increasing numbers of electrons the larger electrostatic forces make it more and more difficult for the atom to revert to that of neon, but tend rather to make the atom take up additional electrons to form a structure like that of argon. According to ordinary potential theory, electrons uniformly distributed throughout a spherical shell should exert no forces on electrons inside the shell, but should repel those outside the shell as though the electrons in the shell were concentrated at the center. On the other hand, an electron in the spherical shell itself is repelled by the others in the shell as if one-half of the other electrons were removed altogether, while the second half were concentrated at the center. Thus let us consider a carbon atom ($N = 6$) which has taken up 4 extra electrons and has completed its octet. An electron in the outside shell is thus attracted by the nucleus which has 6 positive charges, is repelled by the two electrons in the first shell as though they were concentrated at the center, and is repelled by the 8 electrons in the outside shell as if 4 of them were concentrated at the center. The repulsion of the electrons is thus only just able to neutralize the attraction by the nucleus, notwithstanding the fact that the whole atom has an excess of 4 negative charges. If, instead of taking carbon, we had considered nitrogen there would have been a large resulting force tending to hold the electrons even after 3 extra ones had been taken up by the atom. These considerations indicate one of the reasons why the symmetrical arrangements of electrons corresponding to the inert gases have such very great stability and why the elements like oxygen and especially fluorine have such very great tendencies to take up electrons.

According to the above calculation, carbon might just be able to hold 4 electrons, while boron could not do so. In the crude theory just given, however,

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we have neglected to take into account the formation of pairs when electrons are shared between octets or between these and hydrogen nuclei. This will greatly increase the tendency of an atom like that of carbon to take up electrons to complete its octet. For this reason we also find a few boron compounds such as borofluoric acid (HBF_4), metaboric acid, etc., in which the boron atom has an octet. These same arguments apply to such elements as aluminum and silicon.

Atomic Volumes.—The properties of the elements lithium, beryllium, and boron are not as closely related to those of sodium, magnesium and aluminum as these are to potassium, calcium and scandium. Instead we find very marked resemblances between lithium and magnesium, beryllium and aluminum, and boron and silicon. These differences and similarities are due, I think, to the small atomic volumes of lithium, beryllium and boron in their compounds. Before considering these elements individually a discussion of atomic volumes will not be out of place.

The periodic relationships between the atomic volumes of the elements are usually based on the volumes of the free elements in solid or liquid form.[1] Because of the radically different structures which occur among these substances these measurements give very little information in regard to the real volume of the atoms. Thus the structure of fluorine with its diatomic molecules is so different from that of metallic sodium that effects due to the difference in constitution may mask any real changes in the volume of the atoms. This difficulty is largely avoided if we consider the volumes of the atoms in the form of similarly constituted compounds.

In view of the very great stability of the octet in neon it seems probable that the volume of this octet is not materially different from the complete octets in the fluorine and sodium ions. The closeness to which two octets can be made to approach each other however should depend on how great the forces are which draw them together. In liquid neon these forces are weak, so the atoms should be at comparatively great distances. The atomic volume (i.e., atomic weight divided by the density of the liquid) of neon is 19.2. Sodium fluoride consists of sodium and fluorine ions held together in a space lattice by the positive and negative charges. Both ions contain complete octets which differ from those of neon only because of the slightly different charges on the kernels. It may be assumed that the fluorine and sodium octets contribute equally to the molecular volume of sodium fluoride which is 15.2. Thus while in liquid neon the volume is 19.2 in sodium fluoride the volume occupied by each octet is 7.6. It is probable that the volume of the octet itself, that is, the volume of the cube formed by the electrons, is not materially different in the two cases but the strong forces in the sodium fluoride draw the octets closer together. Magnesium oxide whose molecular volume is 11.0, consists of oxygen atoms with a double negative charge and magnesium atoms which have lost two electrons — in

[1] Tables and curves giving these atomic volumes have been given by Harkins & Hall, *J. Am. Chem. Soc.* **38**, 196 (1916).

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both cases giving a simple octet with a structure like that of neon. The volume occupied by each octet is thus 5.5 as compared to 7.6 in sodium fluoride and 19.2 in liquid neon. These results give a measure of the extent to which octets may be made to approach each other more closely by strong forces. Comparing magnesium oxide and sodium fluoride the relative distances between the atoms are as the cube roots of their volumes or as 1 is to 1.114. The ratio of the forces acting between the atoms, taking account of the double charges of the magnesium and oxygen atoms, is as one is to 4.98. Thus for a 5-fold increase in the force, the volume occupied by the octets has decreased 27% (7.6 to 5.5). The atomic volume of metallic sodium is 23.7, greater than even that of neon, notwithstanding the fact that the charges on the electrons and the positively charged sodium ions might be expected to exert strong attractive forces compared to those in liquid neon. It is not reasonable to suppose that the actual volume of the octet of the sodium atoms in metallic sodium is much different from that in sodium fluoride. The large volume of metallic sodium must then be due to a specific repulsion between a completed octet and a single free electron which keeps the electron from approaching the octet. It is probable that this same repulsion is the cause of the remarkable and apparently perfect elasticity of the collisions between electrons and the atoms of the inert gases, or nitrogen.[1] The fact that nitrogen is similar to the inert gases in this respect is additional confirmation of our theory that the nitrogen molecule has a single octet.

It is especially interesting to compare the volume of sodium fluoride with that of metallic sodium for in each case the substance is held together by the forces between particles having unit charges. The volume occupied by the sodium ion in sodium fluoride is 7.6. The free electron in metallic sodium increases this to 23.7 so that the electron seems to require a volume of 16.1, or more than twice that of the octet. However, the effect is probably not quite as great as this for the distance between the positive and negative charges in sodium is some 15% greater than in sodium fluoride. The actual space lattice arrangement of the atoms also needs to be known and taken into account in any proper treatment of this subject. From the molecular volume of magnesium oxide it appears that the atomic volume of the octet is less than 5.5—it is reasonable to assume that with much larger forces it might approach a limiting value of about 4.0. The volume of a single neon octet is thus 6.2×10^{-24} cc. corresponding to a cube having an edge of 1.9×10^{-8} cm.

Assuming the electrons and the sodium ions in metallic sodium to be arranged like the ions of chlorine and sodium in a crystal of sodium chloride, we find that the distance between their centers must be 2.7×10^{-8} cm. Presumably at distances shorter than this the repulsive forces between a single electron and an octet more than compensate for the attraction between oppositely charged univalent ions.

[1] Franck and Hertz, *Verh. deut. physik. Ges.* **15**, 929 (1913).

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According to this view the large atomic volumes of the alkali metals are due to the volumes occupied by single free electrons rather than to a large volume of the atom as such.

Magnesium, although there are two free electrons for each atom, has an atomic volume of 14.0, only a little more than half that of sodium. Comparing this with magnesium oxide, of molecular volume 11, it is clear that the electrons contribute much more to the volume of the metal than does the octet of the oxygen in the oxide. It is probable that the two free electrons form a more or less stable pair and are thus able to occupy a smaller volume than the single electron in sodium.

The atomic volumes of the elements increase at first about in proportion to the atomic numbers and then more slowly. For example, the atomic volumes of the free alkali metals are: lithium 13.1, sodium 23.7, potassium 45.5, rubidium 56.0, and cesium 69.8. The volumes in their compounds are seen from: sodium fluoride 15.2, potassium chloride 37.4, rubidium bromide 51.4, and cesium iodide 57.5. In these compounds the two elements are chosen so as to have as nearly the same atomic numbers as possible. Half of these quantities should give a measure of the maximum atomic volumes of the inert gases lying between them. In this way we find neon 7.6, argon 18.7, krypton 25.7, and xenon 28.7. The molecular volume of lithium fluoride is only 10.0, while that of the fluorine atom alone in sodium fluoride is apparently 7.6. The atomic volume of the lithium nucleus thus must be very small, probably about 2.4. The same rapid increase in atomic volume between the first and second period is observed with the elements in the middle of the period, thus boron 4.7, aluminum 10.4, and carbon 3.4, silicon 11.7.

It seems as though the total volume of the atom tends at first to increase in proportion to the number of electrons. This means that the cells of Postulate 3 have the same volumes even in different atoms in spite of the increasing attraction of the nucleus. However, with larger atomic numbers the rate of increase of volume is much less, and with certain elements like osmium notwithstanding the high atomic number, the atomic volume is so small (8.5) that the hypothesis of constant cell volume seems untenable. It should be noted that the elements of small atomic volume are those in which there are larger numbers of electrons in the outer shell held by attractive forces (Postulate 6) to the underlying electrons. When there are either too few electrons, or when the electrostatic forces predominate, the atomic volume increases.

Let us now continue with a discussion of the properties of individual elements.

Sodium $N = 11$, $E = 1$.—The properties are determined almost solely by the ability of its atoms to give up one electron. It is much more electro-positive than lithium because its atomic volume is greater so that the force with which it holds its electron is smaller.

Magnesium $N = 12$, $E = 2$.—The properties are largely dependent on the ability to give up two electrons. The double charge makes this process

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more difficult than with sodium. There is thus a greater tendency to form insoluble salts and for hydrolysis to occur. Lithium, because of its small volume, holds its electrons more firmly than does sodium, and for this reason resembles magnesium in the solubility of its salts, etc. Magnesium has no tendency to form an octet.

Aluminum $N = 13$, $E = 3$.—The difficulty of giving up 3 electrons to form a positive ion leads to marked hydrolysis and to a tendency to form ensoluble salts. In compounds with oxygen, aluminum probably forms an octet as, for example in $KAlO_2$. If we place $n = 3$, $e = 16$, we find $p = 4$ and are led to the formula $K^+(O = Al = O)^-$. Beryllium, with only two electrons in its outside shell, has a kernel of such small volume that it holds its electrons nearly as firmly as aluminum and therefore resembles aluminum in the solubility of its salts and in other ways.

Silicon $N = 14$, $E = 4$.—This element is no longer able to form positive ions but like carbon, forms practically only compounds in which its atoms have octets. Boron, owing to its small volume, holds its electrons about as firmly as silicon and therefore resembles this element.

The chemistry of silicon compounds is complicated by the marked tendency to form second order compounds. The great number of silicates found in nature seem to be compounds of silicon dioxide with other oxides. The octet theory is applicable to the formation of silicon dioxide and each of the other oxides but not to the minerals resulting from their combination. By far the greater number of such compounds exist in the solid state only. The number of molecules of each of the oxides than can combine together in this way to form crystalline solids is determined mainly by purely geometrical considerations. The writer has already discussed compounds of this kind at some length[1] and Sosman[2] has developed a similar theory.

A compound like hydrofluosilicic acid differs from those we have just considered in that it exists in aqueous solutions. The formation of such compounds is explained by Werner's theory of supplementary valence, but without leading to a definite conception of the mechanism of the combination. We have seen that fluorine has a particularly strong tendency to take electrons outright rather than to share them with other atoms. Thus when fluorine reacts with silicon, 4 fluorine atoms take the 4 electrons from a single silicon atom. The fluorine ions are then held by electrostatic forces and surround the positively charged silicon kernel probably in a tetrahedral arrangement, but without sharing electrons. The electric field is thus almost entirely enclosed within the molecule so the substance SiF_4 is a gas of rather low boiling point. The silicon kernel having as its second shell an octet like that in neon, has a cubic symmetry. There is thus a tendency for the kernel

[1] *J. Am. Chem. Soc.* **38**, 2241 (1916).
[2] *J. Ind. Eng. Chem.* **8**, 985 (1916).

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to take up 6 rather than 4 fluorine ions since these ions can fit opposite the 6 faces of the cube in a very symmetrical way. It may at first seem that a quadrivalent positive ion could not hold 6 negative ions by electrostatic forces but close examination indicates that this arrangement should be possible. Let us assume that a silicon kernel has taken up 6 fluorine ions to form the complex ion SiF_6^{--}. What are the forces acting on each fluorine atom? Let us imagine the fluorine ions at the 6 corners of a regular octahedron with the silicon ion at its center. We will take the distance from the center to the corner of the octahedron as the unit of length. Let us consider the forces acting on one of the fluorine ions which we will denote by A. The attractive force between A and the quadrivalent silicon ion is 4. The repulsive force between A and the fluorine ion farthest from A is $\frac{1}{4}$ since the distance is 2. Each of the other 4 fluorine ions is at a distance $\sqrt{2}$ from A so that the force is $\frac{1}{2}$. But the component in the direction towards the center is only $1/(2\sqrt{2})$. The 4 fluorine ions thus exert a total repulsive force of $2\sqrt{2}$ or 1.41. All 5 thus repel the ion A with a force $1.41+0.25 = 1.66$, while the silicon atom attracts it with a force of 4. Thus notwithstanding the negative charge on the complex ion as a whole, each fluorine ion is attracted to the central nucleus as strongly as it would be to a simple positive kernel having a charge of 2.34 units. The SiF_6^{--} ion can exist as such in solution or can attach to itself two hydrogen ions to form H_2SiF_6.

This simple theory indicates how compounds with a coördination number of 6 can be formed because of purely geometrical and electrical factors. The forces causing such combinations as well as those holding complex silicates, etc., together, will be referred to as secondary valence forces.

The marked contrast between silicon and carbon in their tendencies to form second order compounds is probably due to the larger volume of the

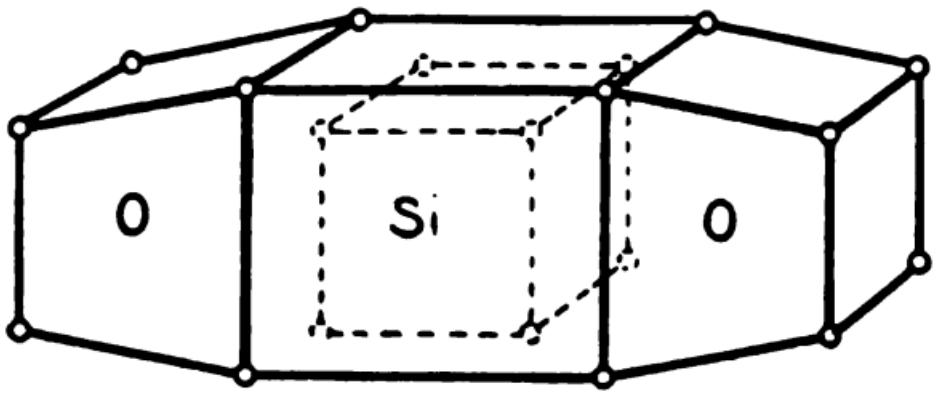

FIG. 14. Diagram of silicon dioxide.

kernel of the silicon atom. This probably greatly decreases the tendency of the silicon atom to hold an octet when combined with oxygen as silicon dioxide. We may picture a molecule of silicon dioxide diagrammatically as in Fig. 14. When a second octet forms around the silicon kernel it would normally have a larger spacing between its electrons than those usual in an oxygen atom. When the silicon and oxygen atoms hold two pairs of electrons

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in common the electrons of the silicon atom are drawn over towards the oxygen. This exposes the positively charged silicon kernel so that a large external field results. This effect is like that caused by the double and especially the triple bonds in organic compounds. There is a continuous series of graduations between a structure of this kind and one in which two oxygen atoms, each with a double negative charge, are held electrostatically by the positively charged silicon kernel. In either case however the oxygen atoms, because of their small number and small volume, are not able to surround the silicon kernel and make its field nearly all internal as is the case in the carbon dioxide molecule. The large external field thus causes molecules of silicon dioxide to be held very firmly to each other or to any other similarly constituted oxides. On the other hand, when oxygen atoms completely surround a kernel of small volume as, for example, in osmium tetroxide, the weak external field causes the substance to have a low boiling point (about 100° for OsO_4). When the silicon atoms combine with the halogens or with hydrogen the larger number of these atoms allows them more nearly to surround the silicon atom and this leads to the formation of liquid and gaseous products, in which secondary valence forces are much less manifest.

Phosphorus $N = 15$, $E = 5$.—The phosphorus atom like that of nitrogen has 5 electrons in its shell. The peculiar arrangement by which two nitrogen atoms form a molecule with a single octet containing an imprisoned pair of electrons is impossible in the case of phosphorus because of the complexity and large volumes of the kernels. Phosphorus therefore cannot form molecules of the composition P_2 except by the structure $P \equiv P$. It also cannot form

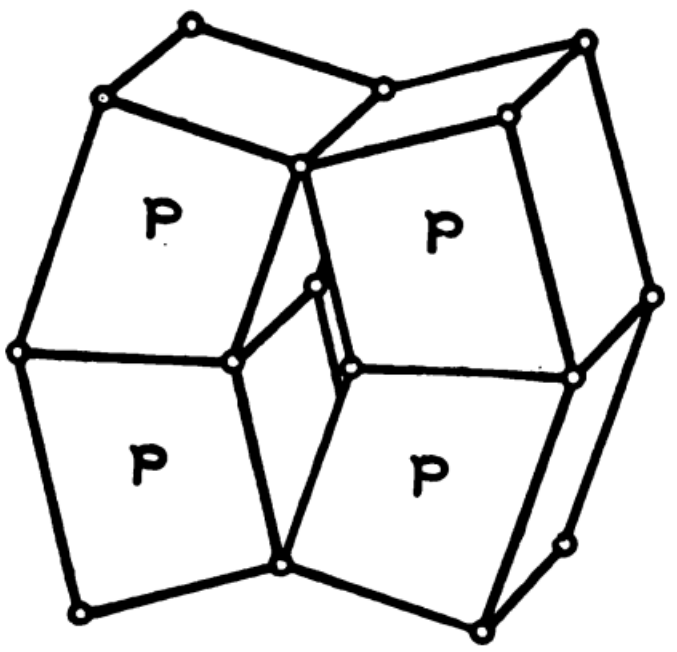

FIG. 15. Diagram of the phosphorus molecule P_4.

P_3 for this involves an odd number of electrons. Let us examine by the octet theory the possibility of forming P_4. Here $n = 4$, $e = 20$ and $p = 6$. The only reasonable ways in which 4 atoms can be arranged sharing 6 pairs are represented by $P = P = P = P$ and $\begin{matrix} P\text{—}P \\ \| \quad \| \\ P\text{—}P \end{matrix}$.

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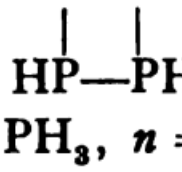
Phosphorus vapor actually has the composition P_4. It is probable from reasons of symmetry that its molecule is represented by the second of the above formulas as indicated in Fig. 15.

Let us now apply the octet theory to the various typical compounds of phosphorus. It will be seen that in every case results are obtained in full agreement with the properties of the compounds without any special assumptions in regard to valence. The structural formulas obtained are in most cases quite different from those derived from the ordinary theory.

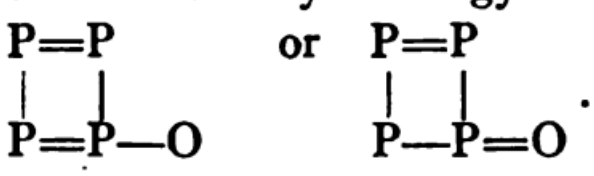
Phosphorus Hydrides, P_4H_2, $n = 4$, $e = 22$, $p = 5$.—This gives by analogy with P_4 the formula



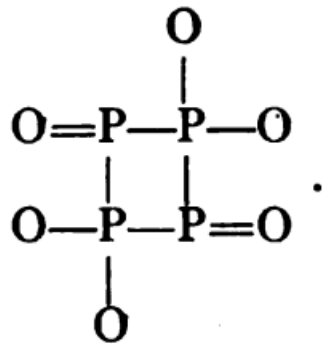
For phosphine, PH_3, $n = 1$, $e = 8$, $p = 0$; hence, PH_3.

For liquid hydrogen phosphide P_2H_4, $n = 2$, $e = 14$, $p = 1$; hence, H_2P-PH_2.

Phosphorus Oxides.—The *suboxide* P_4O gives $n = 5$, $e = 26$ and $p = 7$, for which by analogy with P_4 we find the structural formula to be

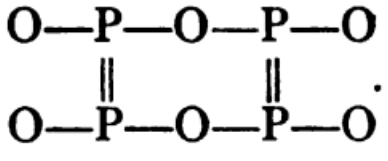


The trioxide has a vapor density corresponding to P_4O_6. This gives $n = 10$, $e = 56$ and $p = 12$. Since this oxide is obtained by the partial oxidation of P_4 and from reasons of symmetry it is probable that its constitution is



In this formula there are 12 pairs of electrons held in common, in accordance with $p = 12$. Each phosphorus atom not only has its octet, but has all 4 pairs of electrons in each of these octets shared by other atoms. We shall see that in practically all phosphorus compounds just as in carbon compounds there is a strong tendency for the 4 pairs in the octet of the central atom to be shared. In fluorine we have noticed just the opposite tendency, namely, not to share any of the pairs with other atoms.

If we represent a molecule of the trioxide by P_2O_3 its constitution can be written O=P—O—P=O. This should be rather unsaturated as compared to the ring since only 3 pairs of electrons around each phosphorus atom are shared. This formula, however, shows the relationship of the trioxide to the acids of phosphorus better does than the ring formula. A reasonable transition between the two structures is



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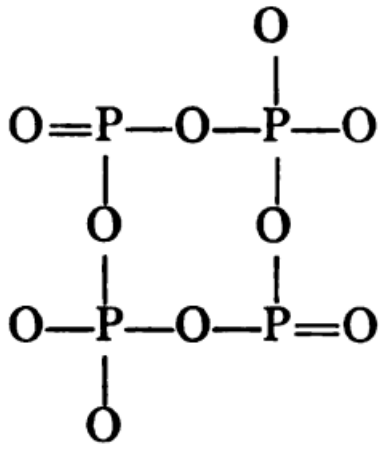
Phosphorus Pentoxide.—The vapor density indicates the formula P_4O_{10}. This gives $n = 14$, $e = 80$ and $p = 16$. From its derivation from P_4O_6, the most probable constitution is

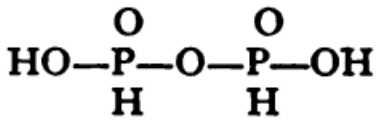
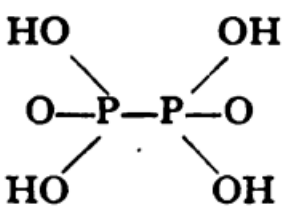
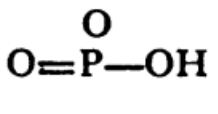
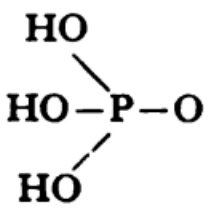
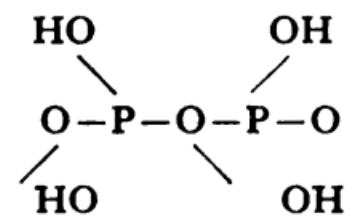


If the formula of the pentoxide is taken as P_2O_5 we can write its formula O=P—O—P=O. It is readily seen that the octet theory indicates that no oxides higher than the pentoxide should exist.

Acids of Phosphorus.—The following table shows the constitution of the various acids as given by the octet theory.

TABLE V

Phosphorous Acids

Name	Formula	*n*	*e*	*p*	Constitution
Hypophosphorous . . .	H_3PO_2	3	20	2	HO—(PH_2)—O
Phosphorous	H_3PO_3	4	26	3	HO—(HP—O)—OH
Pyrophosphorous	$H_4P_2O_5$	7	44	6	
Hypophosphoric	$H_4P_2O_6$	8	50	7	
Metaphosphoric	HPO_3	4	24	4	
Orthophosphoric	H_3PO_4	5	32	4	
Pyrophosphoric	$H_4P_2O_7$	9	56	8	

The constitution as determined from the values of p is shown more clearly in Fig. 16. In each case all 4 pairs of the phosphorus octets are shared by the adjacent atoms. It is significant that these formulas give correctly the number of replaceable hydrogen atoms. Thus hypophosphorous acid is a monobasic

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acid, while phosphorous and pyrophosphorous acids are dibasic. This is readily explainable by the formulas, for it is seen that in the first case two of the hydrogen atoms and in the other cases one atom is bound directly by each phosphorus atom and therefore does not show acid properties.

Phosphorus Chlorides.—For the trichloride PCl_3, we find $n = 4$, $e = 26$ and $p = 3$. The phosphorus octet thus shares a pair of electrons with each of the 3 chlorine atoms. Here is one of the few cases in which the phosphorus atom does not share 4 pairs. It is readily seen from the octet theory, however, that phosphorus could not form a compound PCl_4. Since the chlorine atoms

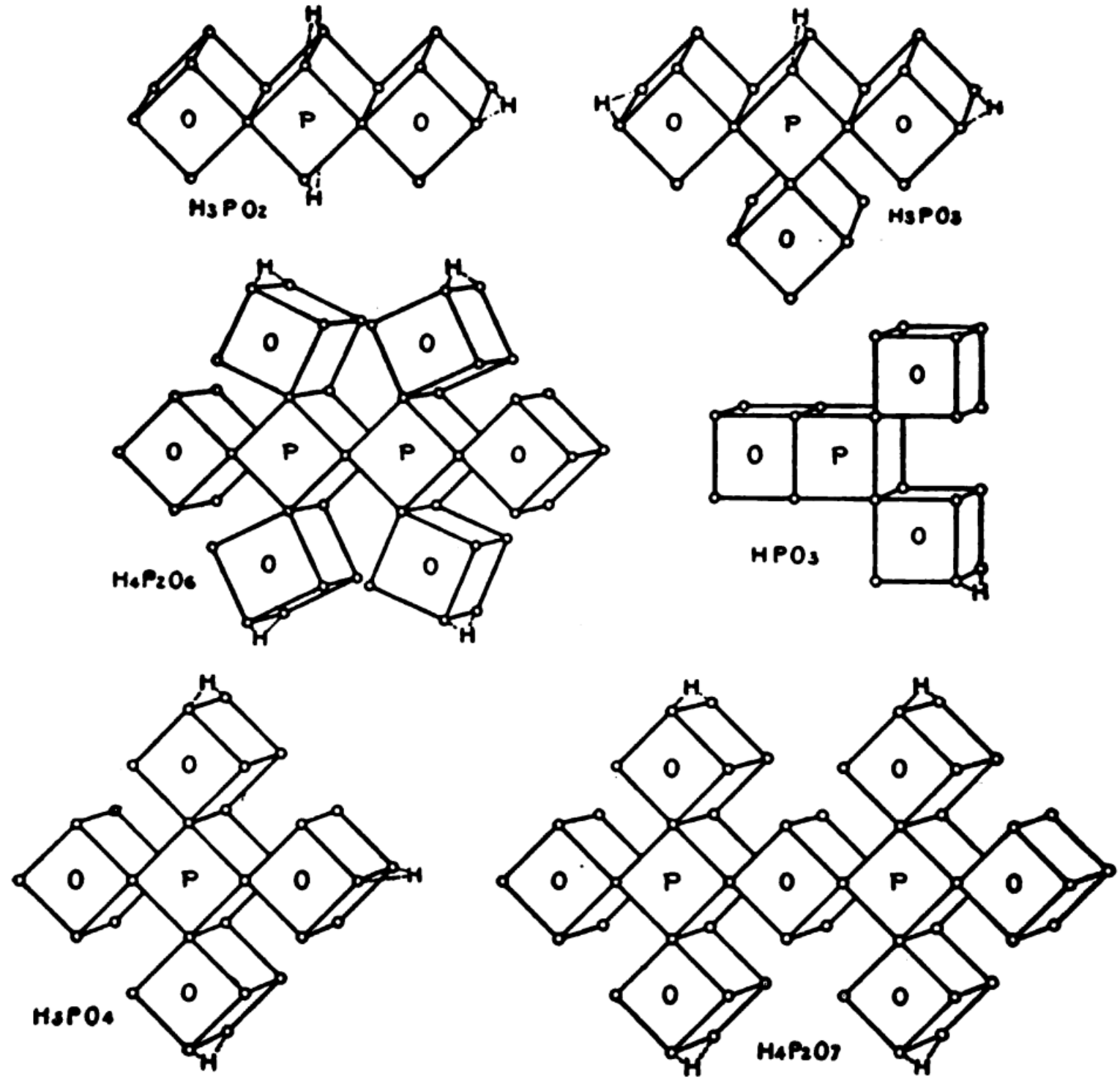

FIG. 16. Diagrams of molecules of phosphorous oxy-acids.

can nearly surround the phosphorus atom and each atom has its octet, the trichloride molecule has a weak external field and hence has a fairly low boiling point (76°).

For phosphorus pentachloride PCl_5, we place $n = 5$, $e = 40$, $p = 0$. This leaves the phosphorus kernel without an octet, the 5 chlorine ions being held by electrostatic attraction. The external field is weak and the substance

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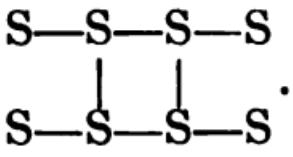
evaporates easily. The tendency of the phosphorus kernel to acquire an octet even if it has to take two electrons from chlorine ions makes this compound dissociate easily into the trichloride and chlorine. If instead of placing $n = 5$ we place $n = 6$, then $e = 40$, and we find $p = 4$. The 5 chlorine atoms cannot share 4 pairs of electrons with the phosphorus octet, but we can imagine that in the solid state of phosphorus pentachloride 4 of the chlorine ions share electrons with the phosphorus octet to form an ion $(PCl_4)^+$, while the other chlorine ion is held in the space lattice by electrostatic forces. It is perhaps probable that the structure of solid phosphorus pentachloride is of this kind. If so, the high melting point (148°) of phosphorus pentachloride compared with the trichloride (−112°) is explained by the large electrostatic forces holding the PCl_4^+ and Cl^- ions to each other and by the symmetry of the PCl_4^+ ion. However, liquid phosphorus pentachloride is a non-conductor of electricity so that in this state only molecules of the type PCl_5 exist.

In the compound $POCl_3$ we find that all the atoms can complete their octets without difficulty. Thus $n = 5$, $e = 32$, $p = 4$ so that each of the 4 atoms shares one pair of electrons with the octet of the phosphorus atom. This is the reason that phosphorus tends so strongly to form this type of compound with the halogens.

Sulfur $N = 16$, $E = 6$.—Since the shell contains 6 electrons like that of oxygen, we might expect sulfur to form a molecule, S_2. At very high temperatures, sulfur vapor has a density corresponding to this formula, but at temperatures a little above the boiling point the vapor consists mostly of S_8, which is also the molecule found from cryoscopic measurements. For this molecule the octet theory gives $n = 8$, $e = 48$, and $p = 8$. By forming a ring compound the 8 electrons can be held together by single pairs of electrons, whereas if we arrange the 8 atoms in a chain there must be one double bond. The ring structure being much more symmetrical is more probable. The most symmetrical formulas seem to be:— I, a continuous ring of 8 electrons arranged in space as shown in Fig. 17. This structure allows the secondary as well as primary valence forces to be satisfied. The molecule probably draws itself together rather more compactly than shown in the figure and thus forms a very symmetrical structure resembling a regular tetrahedron; II, the second possible ring formula is



Although this has a superficial resemblance to the structures best representing the P_4 molecule, it seems unlikely that it corresponds to the constitution of S_8. We shall see that the tendency of the sulfur atoms to form chains is a characteristic property of this element.

Polysulfides.—The tendency by which oxygen atoms attach themselves to each other forming compounds like ozone and hydrogen peroxide, is exhibited in still greater degree by sulfur atoms. Thus there is a series of sulfides

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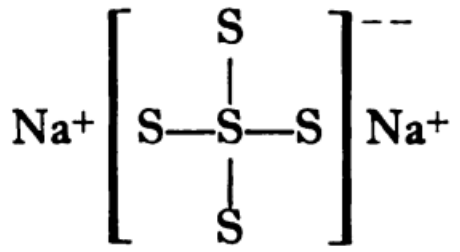
of sodium represented by Na_2S_x where x may have values up to 5. Placing $n = 5$, $e = 32$, and we find $p = 4$. The most probable structure is



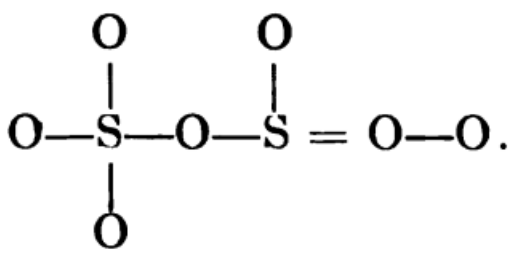
The octet theory thus explains the formation of the sulfides from Na_2S to Na_2S_5 and indicates that more than 5 sulfur atoms in the anion would require a more complicated structure.

Oxides of Sulfur.—For sulfur dioxide we find $n = 3$, $e = 18$, $p = 3$, giving the structure $O = S-O$. For the trioxide, SO_3, we have $n = 4$, $e = 24$, $p = 4$, thus find $O = S\begin{matrix}O\\O\end{matrix}$. This is the most stable oxide because all 4 pairs of electrons of the sulfur octet are shared by the oxygen atoms. It is readily seen from the octet theory that the molecules $O = S\begin{matrix}O\\O\end{matrix}$ should show a tendency to polymerize to form long chains having the structure

The more stable solid modification of sulfur trioxide, which consists of long, fibrous crystals probably has this structure.

The very unstable sesquioxide S_2O_3, which is formed as a blue liquid or bluish green solid, when sulfur is dissolved in liquid sulfur trioxide, at 12°, gives by the octet theory $n = 5$, $e = 30$, $p = 5$. It thus probably has the composition $S-O = S\begin{matrix}O\\O\end{matrix}$ and may thus be regarded as a persulfide of sulfur trioxide. The blue color, which indicates an unstable arrangement of electrons, is probably quite analogous to that produced by the action of hydrogen peroxide on chromates.

Persulfuric anhydride, S_2O_7, is a very volatile liquid which solidifies to a mass of long needles at 0° and decomposes readily into oxygen and sulfur trioxide when heated. The octet theory gives $n = 9$, $e = 54$, and $p = 9$. From this value of p and from the fact that the product is formed by an electric discharge under conditions which yield ozone, the constitution probably is



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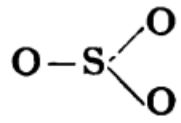
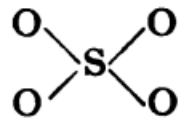
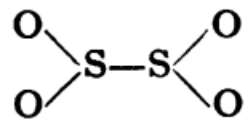
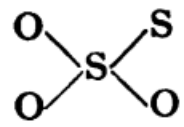
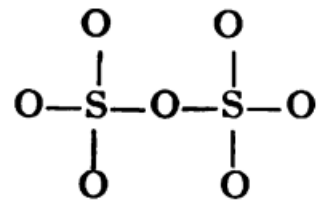
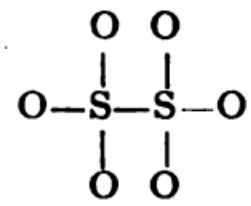
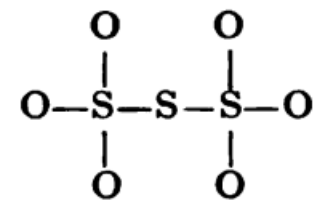
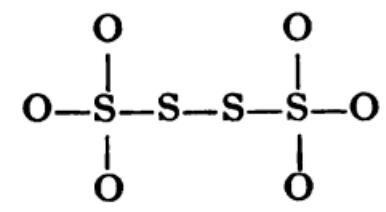
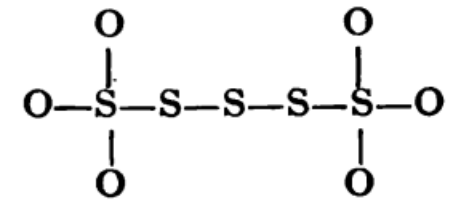
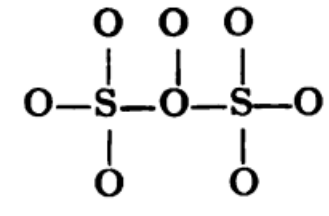
Oxy-acids.—The constitutions of the ions of these acids as found by the octet theory are given in Table VI. The ions rather than the free acids are tabulated because many of the acids do not exist in the free state. In determining the value of e the charge on the ion must be taken into account.

In the more stable acids all 4 pairs of electrons in the octets of the central atoms are shared by the adjoining atoms.

TABLE VI

Ions of the Sulfur Acids

Name of acid	Formula	n	e	p	Constitution
Sulfurous	SO_3^{--}	4	26	3	
Sulfuric	SO_4^{--}	5	32	4	
Hyposulfurous	$S_2O_4^{--}$	6	38	5	
Thiosulfuric	$S_2O_3^{--}$	5	32	4	
Pyrosulfuric	$S_2O_7^{--}$	9	56	8	
Dithionic	$S_2O_6^{--}$	8	50	7	
Trithionic	$S_3O_6^{--}$	9	56	8	
Tetrathionic	$S_4O_6^{--}$	10	62	9	
Pentathionic	$S_5O_6^{--}$	11	68	10	
Persulfuric	$S_2O_8^{--}$	10	62	9	

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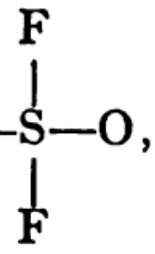
Halogen Compounds.—The most stable chloride of sulfur is S_2Cl_2, for which $n = 4$, $e = 26$, $p = 3$. The constitution is thus Cl—S—S—Cl. The very unstable chloride SCl_2 has the structure Cl—S—Cl. The tetrachloride exists as a solid at very low temperatures and has been said to exist as a liquid at $-20°$, but dissociates rapidly with rise of temperature into chlorine and S_2Cl_2. The octet theory gives for SCl_4, $n = 5$, $e = 34$, $p = 3$. This indicates that 3 chlorine atoms share pairs of electrons with the sulfur atom and form a positive ion $(SCl_3)^+$ while the fourth chlorine atom forms an ion, Cl^-. Since the sulfur atom shares only 3 of its pairs of electrons such a compound should be very unstable. There is however very little evidence that it exists, except in the solid state. It is more probable that a very unstable second order compound between Cl_2 and S_2Cl_2 accounts for the experimental data.

Fluorine has so little tendency to share electrons with other atoms that it forms only one compound with sulfur, namely SF_6. The symmetrical arrangement of the 6 fluorine ions opposite the 6 faces of the octet of the sulfur kernel, and the fact that the fluorine atom and the sulfur kernel are of about the same size, gives the compound SF_6 an extraordinary stability. As a matter of fact, this gas, notwithstanding the large proportion of fluorine in its composition, is a tasteless and odorless gas which is exceedingly stable and inert.

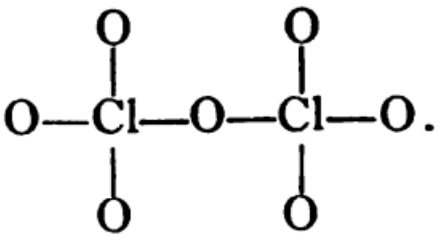
Another tasteless and odorless gas containing fluorine is formed when sulfur dioxide and fluorine are brought into contact with a heated platinum wire. The composition is SO_2F_2. Here $n = 5$, $e = 32$, and $p = 4$. This gives the constitution



in which each fluorine atom shares a pair of electrons with the sulfur atom. In this case the tendency of the fluorine to share electrons has been overcome by the combined tendencies of the sulfur atom to take up an octet and to share all 4 of its pairs of electrons with its neighbors.

Chlorine $N = 17$, $E = 7$.—The essential differences between chlorine and fluorine seem to be due to the more strongly electronegative character of fluorine and its smaller atomic volume. Chlorine, like fluorine, tends to form negative ions, but it differs from fluorine in that it can share electrons with oxygen, especially if at the same time the molecule takes up electrons from some more strongly electro-positive element. It shows a tendency like phosphorus and sulfur to share all 4 pairs of its electrons, if it has to share any.

Oxides of Chlorine.—The monoxide Cl_2O, according to the octet theory, has the structure Cl—O—Cl, since $p = 2$. For the heptoxide Cl_2O_7, we place $n = 9$, $e = 56$, and find $p = 8$, giving the structure



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This is the most stable oxide of chlorine since each chlorine shares 4 pairs of electrons. The peroxide ClO_2, the least stable of the oxides, contains 19 available electrons. It is thus one of the few compounds that have an odd number of electrons. The only other compounds of this kind we have thus far considered, namely nitric oxide and nitrogen dioxide, had in each case one electron too many to form the normal structures. But chlorine peroxide has one electron too few to form a normal compound of the type O—Cl—O. The determination of its structure will be an interesting but probably difficult problem. It is significant that no oxide of chlorine corresponding to NO is known. This is probably due to the fact that a condensed structure like that of nitric oxide, carbon monoxide, etc., is not possible with atoms having an octet in their kernels.

Oxy-acids.—The octet theory explains immediately the chlorine oxy-acids. Thus 4 oxygen atoms can be successively added to the chlorine atom in hydrochloric acid. This gives the acids

$$HCl;\quad HCl{-}O;\quad HO{-}Cl{-}O;\quad HO{-}\overset{\displaystyle O}{\overset{|}{Cl}}{-}O\quad\text{and}\quad HO{-}\overset{\displaystyle O}{\overset{|}{\underset{\displaystyle O}{\underset{|}{Cl}}}}{-}O,$$

corresponding exactly to the acids $HN=O$, $HO{-}N=O$, $HO{-}\overset{\displaystyle O}{\overset{|}{N}}=O$. In each case the octet theory shows why higher acids cannot be formed. In nitric acid and in perchloric acid all 4 pairs of electrons in the octet of the central atom are shared by the adjacent atoms.

First Long Period

Beyond argon we find that the first 3 elements have properties closely related to those of the second short period, but, as was already pointed out in the discussion of the structure of the atoms, these relationships largely disappear beyond titanium. From this point on we find that the octet theory does not apply at all if in calculating e we take the total number of electrons in the shell. For example, all chromic, manganous, ferric and cobaltous salts contain odd numbers of electrons. This difficulty disappears however if in calculating e in Equation 2 we consider only the *available* electrons. We have already discussed why only a certain fraction of the electrons should be available in these elements.

There is nothing arbitrary about this choice of the number of available electrons. In compounds of iron, chromium, manganese, etc., there are fundamental changes in the character of the compounds whenever the number of available electrons changes. Ferrous and ferric salts, for instance, even in the solid state, are as different from one another as though they were salts

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of different metals. Their colors, magnetic properties, chemical properties, etc., are all unmistakably different. But among the elements which precede argon there were no such differences. Thus we cannot satisfactorily divide nitrogen, phosphorus or chlorine compounds into classes according to the valence of their parent atom.

In the compounds of vanadium, chromium and manganese in which these elements enter the acid radical, there seems to be a tendency for the central atom to form octets, although the stability of the octet is much less than those formed by phosphorus, sulfur and chlorine. Thus we repeatedly find compounds, Na_3VO_4, Na_2CrO_4, Na_2MnO_4 and $NaMnO_4$ in which 4 oxygen atoms surround the central atom. Since the free atoms of these elements have little or no tendency to take up electrons to complete their octets, we must conclude that any kernel with a sufficiently large positive charge (5 or more) tends to surround itself with an octet *provided all 4 of the pairs of electrons in this octet are shared by adjoining atoms*. Thus we may speak of an octet being stabilized by the sharing of its pairs.

Among the elements beyond argon it is common to find that a single element forms several acids corresponding to different numbers of available electrons as illustrated, for example, by Na_2MnO_4 and $NaMnO_4$. In the first compound the manganese atom has 6 available electrons while in the second it has 7. We must picture to ourselves the manganese kernel in the first case as consisting of a simple kernel like that of argon, having 7 positive charges, holding a single electron prisoner within the outer octet that is shared by the 4 oxygen atoms.

It is evident that this sort of thing greatly complicates the application of the octet theory. The difficulty, however, is one that is forced upon us by the actual properties of the elements beyond titanium. Complications of this kind are observed especially among such elements as vanadium, chromium, manganese, columbium, molybdenum, tantalum, tungsten and uranium.

Another factor that complicates the chemistry of the elements of high atomic weight is the general tendency to form secondary valence compounds, especially by the elements of small atomic volume, such as those in the so-called eighth group. All the elements of high atomic weight such as antimony, bismuth, selenium, tellurium, iodine and cesium, show very marked tendencies to form secondary valence compounds. A general discussion of this field, however, would be out of place here.

Valence, Coördination Number and Covalence

According to the octet theory each carbon atom in a molecule of an organic substance has an octet and shares all 4 pairs of its electrons with adjacent atoms. For organic compounds, therefore, a pair of electrons held in common by two atoms corresponds exactly to the bond in the ordinary valence

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theory. Among other compounds, however, this relationship does not hold. Thus the octet theory indicates that the nitrogen atom in nitric acid shares 4 pairs of electrons with the oxygen atoms, in other words, the valence of nitrogen is 4. To distinguish between the valence thus found and that assumed in the ordinary valence theory we shall denote by the term "covalence" the number of pairs of electrons which a given atom shares with its neighbors.

Werner's coördination number represents the number of atoms, or molecules, irrespective of their valency, which are arranged in space around a given atom. The *maximum* coördination number for carbon is 4 which is realized in saturated hydrocarbons and halogen compounds. In many organic substances, however, such as carbon dioxide, formaldehyde, etc., the coördination number is less than 4. From the standpoint of the octet theory, the ordinary conception of valence is not definite, but involves at least 3 different properties of the atoms. In tracing general relationships between the elements it has usually been necessary to disregard all valences of the elements, except the maximum positive and negative valences. Now the maximum positive valence is a definite conception — it represents the number of electrons in the shell of the atom. Thus if the element combines with an excess of fluorine or oxygen these elements will usually take all the electrons in the shell. The maximum number of fluorine atoms or twice the maximum number of oxygen atoms thus held is a direct measure of the total number of available electrons in the shell. On the other hand, the maximum negative valence represents the number of electrons which the atom must take up to reach a stable form like that of the inert gases. Both of these conceptions are definite, although quite different. In most compounds, however, the atoms do not take up or give up electrons but rather share them with other atoms.

With carbon it so happens that the number of pairs of electrons shared by other atoms is equal both to the maximum positive and to the maximum negative valence. For other elements, however, there is no necessary relation between the number of pairs of electrons shared and the number of electrons in the shell of the original atom. It is for this reason that the utmost confusion occurs when the ordinary valences are applied to inorganic compounds in which atoms share pairs of electrons.

In using the octet theory to determine the structure of inorganic compounds we determine p in Equation 2 from the total number of available electrons and make no assumptions regarding covalence. This simple theory corresponds with the known facts very much better than the ordinary valence theory, but does not yet accomplish all that could be desired in explaining why certain compounds exist, while others do not. For example, since phosphorus and nitrogen atoms contain the same number of electrons in their shells, the simple octet theory represented by Equation 2, indicates that nitrogen compounds corresponding to all known phosphorus compounds could

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exist and *vice versa*. Thus we might expect the following compounds: H_3NO_4, $Na_4N_2O_7$, P_2O. Similarly because sulfur and oxygen have equal numbers of electrons in their shells we might expect compounds like OS_2, H_2OS_4, OF_6, and O_2Cl_2 corresponding to SO_2, H_2SO_4, SF_6 and S_2Cl_2, respectively.

The octet theory may be made much more useful by supplementing it by a study of the values of the *covalence* as observed for the different elements. We have already noticed that with carbon it is practically always 4 while with fluorine it is usually one or zero. Table VII gives in the column marked *P* a list of the values of covalence corresponding to the elements of the two short periods. The symbol (0+) means that the atom does not share any pairs of electrons with other atoms but has given up one or more electrons and therefore has become positively charged as, for example, in the case of the lithium ion. The symbol (0−) indicates that the atom has taken up electrons to complete its shell but does not share electrons with other atoms, as, for example, the chlorine ion Cl^-.

TABLE VII

Covalence of the First 18 *Elements*

Element	*E* Electrons in shell	*P* Covalence						*S*	Element	*E* Electrons in shell	*P* Covalence						*S*
H	1	(0+)	1	(°−)	.	.	.	.									
He	0	0	..	..	.	.	.	.	Ne	0	0	.	.	.	.	..	.
Li	1	(0+)	..	..	.	.	.	.	Na	1	(0+)	.	.	.	.	..	.
Be	2	(0+)	4?	..	.	.	.	.	Mg	2	(0+)	.	.	.	.	..	.
B	3	(0+)	4	..	.	.	.	.	Al	3	(0+)	4	.	.	.	..	.
C	4	..	4	..	.	.	.	3	Si	4	(0+)	4	.	.	.	..	2
N	5	..	4	3	2	.	.	3	P	5	(0+)	4	3	.	.	..	2
O	6	..	..	3	2	1	.	2	S	6	(0+)	4	3	2	1	(0−)	2
F	7	..	..	..	.	1	(0−)	1	Cl	7	..	4	3	2	1	(0−)	1
Ne	0	0	..	..	.	.	.	.	Ar	0	0	.	.	.	.	..	.

The values of *P* represent the number of *pairs* of electrons which the atom shares with other atoms. In the column marked *S* is given the maximum number of pairs of electrons which an atom is capable of sharing with a single other atom. The values of *P* shown by heavy faced type represent the covalence which occurs in the largest numbers of compounds. Thus for nitrogen in ammonium salts, in nitrates, in N_2O_4, etc., $P = 4$, while in ammonia, nitrous acid, NCl_3, and many organic compounds, etc., $P = 3$.

This table brings out clearly how the covalence of the elements from carbon to fluorine decreases steadily as the number of electrons approaches that of neon. With the corresponding elements of the second short period the lower limits of the covalence decrease as in the first period, but the maximum covalence remains constant at 4. Thus chlorine forms $HClO_4$, but there is no corresponding fluorine compound.

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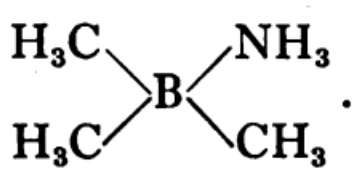
The covalence of an atom is closely related to the coördination number. According to Werner the coördination number is 4 in the following compounds: NH_4Cl, HBF_4, H_2SO_4, H_3PO_4, HPH_2O_2, H_2PHO_3, $HClO_4$, but not in HNO_3, CO_2 or CH_2O. According to the octet theory the covalence of the central atom of all these compounds is 4. In HNO_3, CO_2 and CH_2O one or more of the oxygen atoms is held to the central atom by two pairs of electrons, while in all the others there is never more than one pair of electrons involved in holding together two adjacent atoms. This difference between the octet theory and Werner's theory accounts for many of the cases of unsaturated supplementary valences.

In a very great number of compounds the coördination number and the covalence are identical and the octet theory then corresponds exactly to Werner's theory just as for organic compounds it is equivalent to the ordinary valence theory.

A few examples will make this clear. In the compound HBF_4 we have $n = 5$, $e = 32$, $p = 4$. Each fluorine atom thus shares a pair of electrons with the octet of the boron atom. The covalence of boron is thus 4 in this compound. Similarly for NH_4Cl we place $n = 2$, $e = 16$, $p = 0$. The 4 hydrogen nuclei thus attach themselves to the 4 pairs of electrons in the nitrogen octet making the positive ion NH_4^+. Since the chlorine atom has a complete octet it exists as a negative ion. Therefore ammonium chloride is a salt resembling sodium chloride. In this case also the central atom nitrogen has a covalence of four. These structures correspond exactly to those given by Werner.

An interesting compound whose constitution is not given by the ordinary valence theory is $B(CH_3)_3NH_3$. Applying the octet theory we have $n = 5$, $e = 32$, $p = 4$; whence the structure is



According to the octet theory this is a typical primary valence compound in no way different from organic compounds. It is interesting to note that in this compound the covalence of both the carbon and nitrogen atoms is 4. The structure arrived at is identical with that postulated by Werner except that he assumes that the bond between the boron and the nitrogen corresponds to supplementary valence, while the others are of the primary type. The octet theory indicates that they are all of the same type.

For the compound $B(CH_3)_3$ we place $n = 4$, $e = 24$ and find $p = 4$. But it is not possible to hold 3 methyl groups by 4 pairs of electrons. However, if we place $n = 3$ we find $p = 0$. The structure of this compound therefore must be $B^{+++}[CH_3]_3^-$. Since the volume of the boron atom is small compared with the methyl group and since there are enough methyl groups

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to surround the boron atom, the electric field will be nearly wholly internal and the substance thus has a low boiling point and is not an electrolyte.

The compound $P(CH_3)_3$ gives $n = 4$, $e = 26$, $p = 3$, so that each methyl group shares a pair of electrons with the phosphorus atom. This compound can add itself to methyl iodide to give a compound $P(CH_3)_4I$, for which we find $n = 6$, $e = 40$, $p = 4$. This leads to the structure $[P(CH_3)_4]^+I^-$ in which each of the 4 carbon atoms shares one of the pairs of electrons with the phosphorus atom. The electro-valence of both the carbon and the phosphorus atoms is 4. The structure is quite analogous to that of typical primary valence compounds.

The structures of compounds like $KAuCl_4$, $KBiCl_4$, $K_2Zn(CN)_4$, $Cu(NH_3)_4Cl_2$, K_2NiF_4, $Pt(PCl_3)_2Cl_2$, etc., can be found by the octet theory in the same way. As a final example let us consider the platino-ammonia compounds. In these the platinum is divalent, that is, there are two available electrons in the shell of the atom. For the compound $Pt(NH_3)_4Cl_2$ we place $n = 7$, $e = 48$, $p = 4$. The 4 NH_3 radicals are thus held directly to the platinum each sharing a pair of electrons. This allows the nitrogen and the platinum to have a covalence of 4. The chlorine atoms become ions. For the compound $[Pt(NH_3)_3Cl]Cl$ we place $n = 6$, $e = 40$, $p = 4$. The 3 NH_3 radicals and one of the chlorine atoms are attached to the platinum while the second chlorine forms an ion. The compound $Pt(NH_3)_2Cl_2$ gives $n = 5$, $e = 32$, $p = 4$ so that both chlorine atoms are attached to the platinum. For $K[PtNH_3Cl_3]$ we have $n = 5$, $e = 32$, $p = 4$. All 3 chlorine atoms and the ammonia are attached to the platinum, and the potassium forms a positive ion. In K_2PtCl_4 we find $n = 5$, $e = 32$, $p = 4$ so that all 4 chlorine atoms are held by the platinum while the potassium atoms form positive ion. It will be noted that in each of these compounds the covalence of the nitrogen and the platinum is 4. According to this theory all these compounds should be looked upon as typical primary valence compounds.

Compounds with Coördination Number 6.—The elements of the first short period never have a coördination number greater than 4. This is probably due to the strong tendency to complete the first octet. Among the elements of the second period silicon forms H_2SiF_6 and a few other compounds which show a coördination number of 6 even when these compounds are in solution. Aluminum forms compounds like cryolite, Na_3AlF_6, but this exists only in the solid state. Phosphorus, sulfur and chlorine form no compounds of this kind with the exception of the compound SF_6.

The elements from titanium to nickel and the corresponding elements in the subsequent periods, have especially strong tendencies to form compounds with a coördination number 6. With these elements there is little or no tendency to complete an octet unless all 4 pairs of electrons are shared, so it is not surprising that a larger number of pairs of electrons can also be taken up. We may imagine two ways in which this may occur. It is pos-

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sible that a shell of 12 electrons consisting of 6 pairs tends to form around the central atom. We may call such a group a *disextet*. If m is the number of disextets in a molecule then we have by analogy with Equation 2

$$p = \tfrac{1}{2}(12\,m+8n-e). \qquad (3)$$

We may use this equation for compounds in which one of the atoms has a coördination number 6 in the same way that Equation 2 was used for compounds with coördination number 4.

The other way of looking at these compounds is to consider, as we did in the case of H_2SiF_6, that the central atom does not share any pairs of electrons with the surrounding atoms, but holds these by electrostatic forces. It is evident that there is no difficulty in explaining the structure of K_2PtCl_6 on the assumption that the platinum atom has 4 positive charges and that the 6 chlorine ions are held around it by electrostatic attraction. On the other hand, it is not at first apparent how groups like NH_3, H_2O, etc., can be held by electrostatic forces in compounds like $[Pt(NH_3)_6]Cl_4$ and $PtCl_4(H_2O)_2$. The groups that can enter into compounds in this way are NH_3, H_2O, HCl, PCl_3, etc., in which the covalences are less than 4.

We may look upon each of these groups as consisting of a central octet to which are attached positive radicals. In the cases of NH_3, H_2O and HCl the hydrogen nucleus is the positive element. In PCl_3 the central octet has 8 electrons having a kernel with only 5 positive charges, so that it has a net negative charge of 3 units. Each chlorine atom contributes to this structure 6 electrons and a kernel with 7 positive charges, a net positive charge equal to one.

If we now assume that the positive parts of these added substances are mobile, then when the molecule is brought near a positive charge the central atom is attracted by this while the others are repelled. Thus a molecule of water normally represented by HOH, when it is brought near a positively charged ion will take the form $\begin{matrix}H\\H\end{matrix}\!\!:\!O\ldots Pt^{++++}$. This displacement of the positive charges in the water molecule causes it to be strongly attracted to charged ions, particularly those having large charges.

Because of this effect any highly charged ion, especially if of small volume, can attract molecules of such substances as water, ammonia, etc. The number that can be held depends on geometrical considerations. In view of the more or less cubical form of most atoms and the symmetry with which 6 groups can place themselves it is not surprising that the coördination number of 6 should be so common.

By either of these theories we can account for the structure of practically all complex compounds having a coördination number 6. The second of these theories explains also the few cases in which the coördination number has values other than 4 or 6.

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General Conclusions

The theory of atomic structure advanced in the present paper not only explains in a satisfactory manner the general properties and relationships of all the elements, but also gives a theory of the formation and structure of compounds which agrees excellently with the facts. It leads directly to a valence theory for organic compounds which is the exact equivalent of the ordinary theory. When applied to the structure of complex inorganic compounds it leads to a theory practically identical with that of Werner. In cases like those of the oxides of nitrogen, etc., which have not previously been explained by any theory of valence the results are thoroughly satisfactory. The structure of the nitrogen, carbon monoxide and hydrocyanic acid molecules are accounted for and new relationships are obtained.

Under these conditions the postulates underlying the theory receive strong support. In fact, the results seem to establish the fundamental correctness of most of the postulates. The recent advances in the physics of the electron have been largely along the lines of Bohr's theory. It is generally assumed that the electrons are revolving all in one plane, in orbits about the nucleus. Such a view is wholly inconsistent with that of the present paper. Bohr's theory has had marked success in explaining and even in predicting new facts connected with the spectra of hydrogen, helium and lithium, and must therefore contain important elements of truth.

It will probably be possible to reconcile the two theories. As has already been pointed out, Bohr's stationary states have a close resemblance to the cells postulated in the present theory. The series of numbers 1, $\frac{1}{4}$, $\frac{1}{9}$, $\frac{1}{25}$ occur in much the same way in both theories.

The cellular structure postulated here also seems to be closely related to J. J. Thomson's[1] theory of atomic structure in which he postulates tubes of force. It seems as though each cell in the present theory is analogous to the inner end of one of Thomson's cylindrical tubes of force. This view suggests that in an atom the electrons are acted on by a repulsive force inversely proportional to the cube of the distance from the nucleus and an attractive force proportional to $1/\tau^2$ where τ is the index number of the shell in which the electron is located. Thus instead of the force varying continuously, as in Coulomb's law, it varies discontinuously in proportion to 1, $\frac{1}{4}$, $\frac{1}{9}$, $\frac{1}{25}$, etc., and only at large distances where τ is very large does the force vary approximately continuously. In some such way we may hope to be led to a modification of Bohr's theory in which the electrons do not rotate about the nucleus.

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[1] *Phil. Mag.* **26**, 792, 1044 (1913).

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Summary

The theory presented in this paper is essentially an extension of Lewis'[1] theory of the "cubic atom". It may be most concisely stated in terms of the following postulates:

1. The electrons in atoms are either stationary or rotate, revolve or oscillate about definite positions in the atom. In the most stable atoms, namely those of the inert gases, the electrons have positions symmetrical with respect to a plane, called the equatorial plane, passing through the nucleus at the center of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) perpendicular to this plane through which 4 secondary planes of symmetry pass forming angles of 45° with each other. These atoms thus have the symmetry of a tetragonal crystal.

2. The electrons in any given atom are distributed through a series of concentric (nearly) spherical shells, all of equal thickness. Thus the mean radii of the shells form an arithmetric series 1, 2, 3, 4, and the effective areas are in the ratios $1:2^2; 3^2; 4^2$.

3. Each shell is divided into cellular spaces or cells occupying equal areas in their respective shells and distributed over the surface of the shells according to the symmetry required by Postulate 1. The first shell thus contains 2 cells, the second 8, the third 18, and the fourth 32.

4. Each of the cells in the first shell can contain only one electron, but each other cell can contain either one or two. All the inner shells must have their full quotas of electrons before the outside shell can contain any. No cell in the outside layer can contain two electrons until all the other cells in this layer contain at least one.

5. Two electrons in the same cell do not repel nor attract one another with strong forces. This probably means that there is a magnetic attraction (Parson's magnetic theory) which nearly counteracts the electrostatic repulsion.

6. When the number of electrons in the outside layer is small the arrangement of the electrons is determined by the (magnetic?) attraction of the underlying electrons. But when the number of electrons increases, especially when the layer is nearly complete, the electrostatic, repulsion of the underlying electrons and of those in the outside shell becomes predominant.

7. The properties of the atoms are determined primarily by the number and arrangement of electrons in the outside shell and by the ease with which the atom is able to revert to more stable forms by giving up or taking up electrons.

8. The stable and symmetrical arrangements of electrons corresponding to the inert gases are characterized by strong internal and weak external fields of force. The smaller the atomic number, the weaker the external field.

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[1] *J. Am. Chem. Soc.* **38**, 762 (1916).

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9. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by: (*a*) a single hydrogen nucleus; (*b*) two hydrogen nuclei; (*c*) a hydrogen nucleus and the kernel of another atom; (*d*) two atomic kernels (very rare).

10. The next most stable arrangement of electrons is the *octet*, that is, a group of 8 electrons like that in the second shell of the neon atom. Any atom with atomic number less than 20, and which has more than 3 electrons in its outisde layer tends to take up enough electrons to complete its octet.

11. Two octets may hold one, two, or sometimes 3 pairs of electrons in common. One octet may share one, two, 3, or 4 pairs of its electrons with one, two, 3, or 4 other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets.

This theory explains the periodic properties of all the elements including those of the eighth group and the rare earths. It meets with success in explaining the magnetic properties of the elements, and applies as well to the so-called physical properties, such as boiling points, freezing points, electric conductivity, etc., as it does to the "chemical properties". It leads to a simple theory of chemical valence for both polar and non-polar substances. In the case of organic compounds the results are identical with those of the ordinary valence theory, while with oxygen, nitrogen, chlorine, sulfur, and phosphorus compounds, the new theory applies as well as to organic compounds, although the ordinary valence theory fails nearly completely.

This theory explains also the structure of compounds which, according to Werner's theory, are second order compounds with a coördination number equal to 4. According to the present theory, such compounds are to be regarded rather as typical primary valence compounds.

This valence theory is based on the following simple equation:

$$e = 8n - 2p$$

where e is the total number of available electrons in the shells of all the atoms in a molecule; n is the number of octets forming the outside shells, and p is the number of pairs of electrons held in common by the octets. This equation is a complete mathematical statement of the primary valence requirements, not only in organic, but in inorganic chemistry.

The theory leads to very definite conceptions as to the positions of the electrons in the molecules or space lattices of compounds. The structures of molecules of nitrogen, carbon monoxide, hydrogen cyanide, and NO prove to be exceptional in that the kernels of both atoms in the molecule are contained within a single octet. This accounts for the practically identical "physical" properties of nitrogen and carbon monoxide, and for the abnormal inertness of molecular nitrogen.

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The results obtained by the use of the postulates are so striking that one may safely reason that the results establish the fundamental correctness of the postulates.

These conclusions, however, are not easily reconciled with Bohr's theory of the atom. Bohr's stationary states have a rather close resemblance to the cellular structure postulated in the present theory. There are also striking points of similarity with J. J. Thomson's theory of the structure of atoms, in which he assumes that the attractive forces are limited to certain tubes of force.

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THE OCTET THEORY OF VALENCE AND ITS APPLICATIONS WITH SPECIAL REFERENCE TO ORGANIC NITROGEN COMPOUNDS

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THE OCTET theory of valence[1] leads to structural formulas for organic compounds which are identical with those given by the ordinary valence theory whenever we can assume a valence of 4 for carbon, 3 for nitrogen, 2 for oxygen and one for hydrogen and chlorine. This follows from the following reasoning:

Let us represent by E the number of electrons in the shell of an atom. For the elements of the two short periods E is equal to the ordinal number of the group in the periodic system. Thus for hydrogen and sodium $E = 1$, for carbon $E = 4$, for nitrogen and phosphorus $E = 5$, for oxygen and sulfur $E = 6$ and for chlorine $E = 7$.

We represent by e the total number of electrons in the shells of the atoms that combine to form a molecule. Let n be the number of octets formed from these electrons, and let p be the number of pairs of electrons which the octets share with one another. Since every pair of electrons thus shared reduces by two the number of electrons required to form the molecule, we are led to the "octet equation".

$$p = \tfrac{1}{2}(8n - e). \qquad (1)$$

Each pair of electrons held in common by two octets corresponds to a covalence bond. In addition to bonds given by this equation there are those corresponding to pairs of electrons which hold hydrogen nuclei. Thus if H represents the number of hydrogen atoms in a molecule, the total number of covalence bonds v in the molecule is

$$v = p + H. \qquad (2)$$

Let C, N, X and Cl represent, respectively, the numbers of carbon, nitrogen, oxygen and chlorine atoms in the molecule. Equation 1 thus gives

$$2p = 8(C+N+X+Cl) - (4C+5N+6X+7Cl+H). \qquad (3)$$

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[1] G. N. Lewis, *J. Am. Chem. Soc.* **38**, 762 (1916); Langmuir, *Ibid.* **41**, 868, 1543 (1919); and *Proc. Natl. Acad. Sci.* **5**, 252 (1919).

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Simplifying and substituting in (2) we obtain

$$2v = 4C+3N+2X+Cl+H. \qquad (4)$$

We are also led to this equation if we calculate, by the ordinary valence theory, the total number of valence bonds in a molecule, assuming the valences to be, respectively, 4, 3, 2 and 1 for carbon, nitrogen, oxygen and chlorine. These valences are Abegg's countervalences and are each equal to $8-E$. The factor 2 in the first term of Equation (4) results from the fact that in adding $4C$, $3N$, etc., we count each bond twice.

It is thus proved that any formula written in accordance with the ordinary valence theory will be in agreement with the octet theory, if we take the valence of hydrogen as unity and that of each other atom as $8-E$. On the other hand, it is apparent that with valences other than $8-E$, the ordinary valence theory leads to results different from those of the octet theory. It is the object of this paper to deal especially with cases of this kind.

As the first example, let us consider sodium chloride. For sodium $8-E$, is 7 while the ordinary valence theory assumes a valence of unity. Applying the octet theory to sodium chloride, we place $e = 1+7 = 8$. The chlorine atom forms an octet, but we cannot reasonably assume that the sodium takes up 7 more electrons to complete an octet. Therefore, $n = 1$ and Equation (1) gives $p = 0$. The covalences of chlorine and sodium in this compound are thus each zero. But since $n = 1$ the chlorine atom must have a complete octet and must, therefore, be negatively charged. Similarly the sodium atom, having lost its extra electron, will be positively charged. The atoms are held together by electrostatic forces even without sharing electrons. This result is eminently satisfactory, for it explains at once why X-ray crystal analysis gives no evidence of molecules of sodium chloride, and why salt is ionized in water solutions and in the molten state. This theory, however, does not indicate that sodium and chlorine ions should never be held together in pairs. The vapor of sodium chloride and solutions in non-ionizing solvents may well contain such pairs or molecules held together by the attraction of the ions, but even in this case the covalence would be zero. This conception seems more useful than one in which the valence is taken as the number of electrons transferred from one atom to the other. In the cases just considered it is so obvious that the two ions will tend to be drawn together by their electrostatic attraction, that we hardly need to use the conception of valence to describe the attraction.

This theory is in full accord with the theory of S. R. Milner[1] in which he argues that the ions in solutions of strong electrolytes are never associated into molecules, but that pairs of ions which are temporarily near together may act as if bound together electrostatically. This theory explains the failure of Ostwald's dilution law for strong electrolytes, and is quantitatively in agreement

[1] *Phil. Mag.* **35**, 214, 354 (1918).

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with the best experimental data on the conductivity of electrolytes. Almost identical theories of strong electrolytes have been developed recently by Bjerrum[1] and by Ghosh.[2]

As a second example let us consider the structure of ammonium chloride, a typical case in which the nitrogen is certainly not tervalent. Here $e = 16$, $n = 2$ and we obtain by Equation 1, $p = 0$. This means that the nitrogen and the chlorine octets do not hold electrons in common. If we consider that the 4 hydrogen nuclei are at first detached from the nitrogen and chlorine octets, then the nitrogen atom would have an excess of 3 negative charges, and the chlorine one negative charge. The hydrogen nuclei can distribute themselves between the two octets in such a way as to render them electrically neutral if 3 hydrogen nuclei are bound by 3 pairs of electrons in the nitrogen octet, while the fourth hydrogen nucleus goes to the chlorine. This gives a mixture of ammonia and hydrochloric acid gases and corresponds with the facts observed at high temperatures. On the other hand, since the more electronegative chlorine has the lesser tendency to share its electrons, the 4 hydrogen nuclei can attach themselves to the 4 pairs of electrons of the nitrogen octet forming a very symmetrical positive ion, while the chlorine remains as a negative ion. The ammonium ion and the chlorine ion thus have covalences of zero, but that of the nitrogen atom is 4. The structure of the ammonium ion is thus exactly like that of the methane molecule except for the difference in the charge on the nucleus. The relationship between the ammonium ion and methane is described by the term isosterism and this conception proves of value in correlating the similarity between the potassium and the ammonium ions with that between argon and methane.[3] The same kind of reasoning can be used to explain the fact that the ammonium ion resembles the potassium ion more closely than it does the sodium ion. The sodium ion has a structure like the neon atom, but neon differs from methane much more than argon does, so we should expect the sodium ion to show similar differences from the ammonium ion. The low boiling points of argon and methane show that the external field around these molecules (or atoms) must be very small. There should then be no strong forces around the potassium and ammonium ions except those due to the electrostatic charge. The markedly different properties of the silver ion proves that in other cases there are forces of a different kind which are of importance in determining the properties. The silver ion is related to the palladium atom as the potassium ion is to argon, and the great difference between argon and palladium corresponds to the difference between the potassium and silver ions.

From the examples just cited it is clear that the octet theory applies satisfactorily even when the valence of atoms is not equal to $8-E$. In these cases

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[1] *Z. Elektrochem.* **24**, 321 (1918).
[2] *J. Chem. Soc. Trans.* **113**, 449, 627 (1918).
[3] *J. Am. Chem. Soc.* **41**, 1547 (1919).

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structural formulas are obtained quite different from those the ordinary valence theory of organic chemistry, but they are in perfect agreement with the properties of the compounds. It is true that Werner's theory leads to the correct constitution of ammonium compounds, but only by making a large number of assumptions of a quite different kind from those on which the organic structural formulas are based. The particular merit of the octet theory is that it gives a single simple theory which includes the extreme types of compounds represented by organic compounds, the alkali halides, and so-called complex compounds.

The octet theory as expressed by Equation (1) is, of course, not capable of showing distinctions between compounds of two elements which have the same number of electrons in their shells, as for example between nitrogen and phosphorus. However, as was pointed out in the previous paper, the theory can be supplemented by certain more or less empirical rules regarding the covalence of the various elements. The general study of compounds by the octet theory has shown the following covalences:

The inert gases, alkali and alkaline earth metals, zero. Carbon, 4 in all ordinary organic compounds, but in some cases the covalence may be 3 as for example in calcium carbide, triphenylmethyl sodium and many other triphenylmethyl derivatives. Nitrogen, usually 3, but 4 in most compounds where quinquevalent nitrogen has been assumed, and 2 in a few compounds. Oxygen, 1, 2 or sometimes 3 (in peroxides). Fluorine, zero or 1. Phosphorus, usually 4, sometimes 3 and rarely zero. Sulfur and chlorine may have any values from zero to 4.

According to the ordinary theory the valences of an element usually increase by steps of two, thus nitrogen and phosphorus are supposed to have valences of 3 and 5; sulfur, 2, 4 and 6; chlorine, 1, 3, 5 and 7, etc. According to the octet theory, however, where the covalence is variable, its value increases by steps of one. The double steps of the ordinary theory are due to the fact that the total number of electrons, e, must be an even number according to Equation (2), so that where univalent elements are added two atoms must be added at a time. It is well known that oxygen atoms are added singly as in HNO_2, HNO_3, $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$. The ordinary theory assumes that these are held by double bonds, while the octet theory shows that they are held by single pairs of electrons.

Tercovalent Nitrogen

It was shown by Equation (4) that the structural formulas written according to the ordinary theory are always in accord with the octet theory when the valence of nitrogen is 3. Let us see, however, what light the octet theory throws on the stereoisomerism of nitrogen compounds.

In the previous paper reasons were given for believing that when the 8 electrons in an octet are not shared by other atoms they are normally arranged at the corners of a cube. A pair of electrons held in common by two atoms,

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however, acts as though it were located at a point. When an atom has a covalence of 4 the 8 electrons in its octet are, therefore, drawn together into 4 pairs which arrange themselves symmetrically at the corners of a regular tetrahedron. As Lewis already pointed out, stereoisomerism of carbon compounds is thus fully explained. The same reasoning applies to atoms of nitrogen, phosphorus, sulfur, etc., whenever these atoms are quadricovalent, so that stereoisomers are obtained under the same structural conditions as with carbon compounds. The experimental facts are in full accord with this conclusion.

When only 3 pairs of electrons in an octet are shared we should expect an arrangement like that shown diagrammatically in Fig. 1.

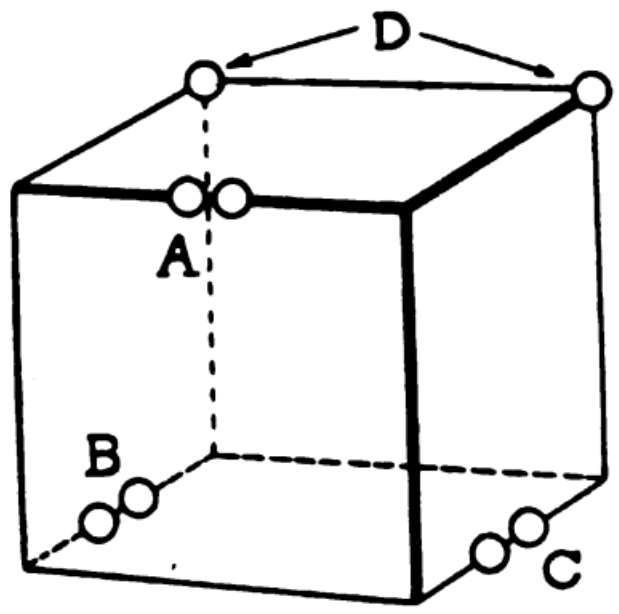

FIG. 1.

The 3 pairs of electrons, A, B and C, which correspond to the 3 covalence bonds are arranged in space approximately like 3 of the corners of a regular tetrahedron. The fourth corner corresponds to the unshared pair, D. This arrangement of the 3 bonds in space agrees exactly with Hantzsch and Werner's[1] theory which has so well explained the isomerism of aldoximes, ketoximes, hydrazones, osazones, diazo compounds, etc. Neogi's recent theory[2] assumes an identical arrangement of the valence bonds. For a full discussion of the evidence in favor of this arrangement Neogi's paper should be consulted.

The absence of isomers among amines containing 3 different groups is not inconsistent with this theory, for it can be satisfactorily explained by a mobility of the groups caused by the presence of the unshared pair of electrons at D. Thus, in a compound $NR_1R_2R_3$ each of the 3 alkyl groups holds a pair of electrons in common with the nitrogen atom, but the nitrogen atom has another pair of electrons (D in Fig. 1) which is not shared. We may assume that the alkyl groups are able to shift into the unoccupied position while the pair of electrons has mobility enough to allow it to occupy the position just vacated by the alkyl group. This could occur without the alkyl radical becoming

[1] *Ber.* **23**, 11 (1890).

[2] *J. Am. Chem. Soc.* **41**, 622 (1919).

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detached from the nitrogen atom at any time. A similar mobility would not exist if all 4 pairs of electrons were shared. Stereoisomers among compounds of tervalent nitrogen are observed only when the nitrogen is held by a double bond, that is, when two of its pairs of electrons, as for example B and C in Fig. 1, are shared by a single other atom. Such a behavior seems quite reasonable on the basis of this structure. With the double covalence bond it is natural that new constraints should be called into existence in the atom and that the mobility of its other electrons should be decreased.

Quadricovalent Nitrogen, Etc.

The structure of tetramethyl ammonium hydroxide, $(CH_3)_4NOH$ is found by placing $e = 40$; $n = 6$ which gives $p = 4$. The nitrogen is thus quadricovalent (as in the ammonium ion) and the hydroxyl ion exists as a negative ion which does not share electrons with the ammonium radical. It is thus completely ionized in solution and is, therefore, a strong base. Of course any other negative ion can take the place of the hydroxyl ion.

In applying the octet theory to the structure of organic compounds it is usually convenient to consider the different parts of molecules separately. We can accomplish this by letting R, R′, etc., represent univalent radicals and assuming that for each radical $E = 7$ and $n = 1$. For example, the radical C_3H_7 in a molecule really contributes 19 electrons to e and 3 octets to n. If we replace this by R we add only 7 electrons to e instead of 19 and one octet to n instead of 3. This decreases n in Equation (2) by 2 units and decreases e by 12 units. The result is that the value of p found by the equation is decreased by 2 units, i.e., $\frac{1}{2}$ (16–12). But since 2 pairs of electrons must be shared between octets in C_3H_7 while none are needed for R, it is evident that we have not affected the value of p for the remainder of the molecule by substituting R for C_3H_7. This reasoning will be found to hold whenever R represents any univalent radical. For a divalent radical we can place $E = 6$, $n = 1$.

According to this theory the substituted ammonium compounds should show isomerism exactly like that of carbon compounds, since the nitrogen is quadricovalent. This is in full accord with Werner's theory and with all the experimental data. Neogi[1] raises an objection to Werner's theory on the grounds that the latter "has postulated the existence of as many as three kinds of valence, viz., (1) principal, (2) subsidiary valences of nitrogen, and (3) residual valence of the ammonium group." It is seen that the present theory reaches a conclusion essentially similar to Werner's without making any additional assumptions regarding valence. The octet theory thus removes the objections that have been raised against Werner's theory. Neogi's own assumption of a tetrahedral nitrogen atom is, of course, in full agreement with the octet theory, but his assumption of a fifth bond "attached to the nitrogen by principal valences,

[1] *Loc. cit.* p. 623.

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though four of them are in the inner zone and the fifth is in the outer zone" is entirely unnecessary and introduces needless complication. Neogi states that "there is no escape from acknowledging the pentavalence of nitrogen as in the amine-oxides $O:NR_1R_2R_3$." The octet theory gives for the amine-oxides $e = 32$, $n = 5$ and $p = 4$. Thus the nitrogen is quadricovalent, and it is entirely unnecessary to assume quinquevalent nitrogen. The octet theory thus greatly simplifies our conception of the structure of compounds of this type. The amine oxides should, of course, exist in two optically isomeric forms whenever the 3 substituted radicals are different, just as in other cases of quadricovalent nitrogen. Neogi by arbitrary assumptions explains the isomerism of these oxides, but states that none of the other theories of the stereoisomerism of nitrogen compound is able to do so.

The isomeric compounds $(Me_3NOR)OR_1$ and $(Me_3NOR_1)OR$ prepared by Meisenheimer[1] are satisfactorily explained by the octet theory. One of the OR radicals exists as a negative ion as in the alcoholates, while the other shares a pair of electrons with the nitrogen atom.

One fundamental objection to Neogi's theory is that it gives no adequate reason why only radicals capable of forming *negative* ions can be held by the fifth bond.[2]

The octet theory throws a great deal of light on the properties of ammonium compounds. Since in typical ammonium salts the NH_4 group exists as an ion, the physical properties should resemble potassium salts for the reasons already given. The close relationship between the solubilities, crystalline forms, etc., of ammonium and potassium salts is in fact very striking, but in certain other respects such as vapor pressures, melting points, etc., there are often striking differences. Ammonium chloride sublimes without melting at about 340° at atmospheric pressure, while the corresponding potassium salt melts at 772°, and boils only at very much higher temperatures. It is probable that this difference is due to the dissociation into ammonia and hydrogen chloride although this simple assumption does not wholly account for the facts since perfectly dry ammonium chloride is said to vaporize without dissociation. However, the total vapor pressure at a given temperature has been found to be the same whether or not the vapor is dissociated.[3] This seemingly incomprehensible result probably indicates that something closely related to dissociation does occur even when the vapor density corresponds to that of ammonium chloride, and that in any case the so-called "undissociated" vapor probably has molecules

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[1] *Ann.* **397**, 273 (1913).

[2] The absence of optical isomers of the substituted pyridinium and quinolinium compounds referred to by Neogi on p. 638 of his paper is undoubtedly to be explained by an effect in the pyridine ring similar to that which prevents the occurrence of two isomers of *o*-dichlorobenzene such as might be expected from the Kekulé formula.

[3] Abegg, *Z. physik. Chem.* **61**, 455 (1908), and subsequent papers by van Laar, Wegscheider and Scheffer.

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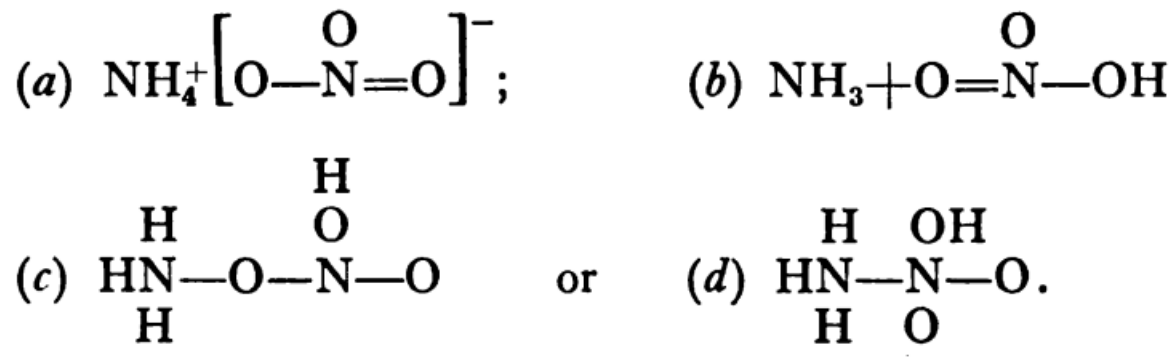
of a quite different structure from those that would be obtained from potassium chloride. It would seem that a study of the dielectric constants of the "dissociated" and "undissociated" vapors and possibly their electric conductivities or ionizing potentials might clear up these puzzling questions.

The failure to obtain the ammonium halides in the molten condition is what is to be expected by the octet theory.[1] There are, however, other ammonium salts which melt at rather low temperatures compared to the corresponding potassium salts. As examples let us consider ammonium nitrate which melts at 166° while potassium nitrate melts at 337°, and ammonium trinitride, NH_4N_3, which melts at 110°.

Applying the octet equation to ammonium nitrate we find $p = 4$. This leads to the following possible arrangements:



Structure (*a*) corresponds to the salt type; this should have a melting point comparable with that of potassium nitrate.

Structure (*b*) corresponds to a possible dissociation into nitric acid and ammonia.

Structures (*c*) and (*d*) suggested by the octet theory are quite inconsistent with the ordinary valence theory. The melting of anhydrous ammonium nitrate perhaps depends, however, upon the formation of one or both of these tautomeric products.

Upon heating, (*c*) should give $2H_2O+N=O=N$, while (*d*) should give $2H_2O+N=N=O$. These constitutions thus explain the formation of nitrous oxide.

We shall see from data to be given further on that there is good evidence that nitrous oxide is represented by the structure $N=N=O$. Therefore,

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[1] With the assistance of Miss Katharine Blodgett, I have found that pure ammonium chloride, sealed up in a small, heavy-walled Pyrex glass tube and heated, melts to a clear liquid at about 550°. By plotting the logarithms of the vapor pressures, measured by Smith and Calvert, *J. Am. Chem. Soc.* **36**, 1373 (1914), against the reciprocals of the corresponding absolute temperatures a straight line was obtained. Extrapolation along this line gives the vapor pressure of ammonium chloride at 550° as 66 atmospheres. The ratio between the melting point of ammonium chloride (823°K) and that of potassium chloride (1045°K) is not greatly different from the ratio between the melting point of ammonium hydrogen sulfate (413°K) and that of potassium hydrogen sulfate (473°K). The lower melting point of the ammonium salts and their somewhat greater solubilities are probably to be accounted for by the tetrahedral shape of the ammonium ion (like that of the methane molecule) as compared to the cubical shape of the potassium ion.

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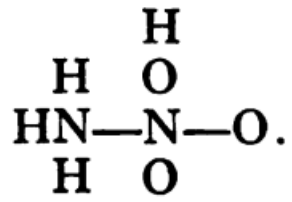
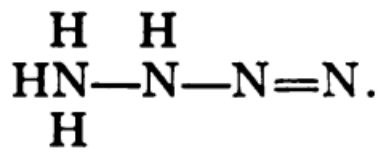
molten ammonium nitrate probably contains some molecules having the structure



It is to be expected that molecules of this type have relatively weak external fields of force as compared to $NH_4^+.NO_3^-$.

In a similar way the melting of NH_4N_3 at 110° is, perhaps, to be ascribed to the formation of molecules of the structure



According to the above hypothesis the difference between the melting points of the ammonium salts and the corresponding potassium salts is dependent on the presence of double bonds in the anion of the acid. Ammonium sulfate has an anion in which there are no double bonds, and the central atom has a covalence of 4. It is, therefore, not possible for the ammonia group to attach itself to the sulfate ion in the same manner as with the nitrate ion. Therefore, we should expect ammonium sulfate to have a melting point only a little lower than that of potassium sulfate (1072°). Now most tables of physical constants and handbooks like Abegg's give the melting point of ammonium sulfate as 140°. These statements seemed so radically inconsistent with the octet theory that I was led to test the data by experiment. It was found that ammonium sulfate remained practically unchanged until heated to about 280° and it then decomposed, giving off ammonia and yielding fused ammonium hydrogen sulfate. Subsequently I found that Reik[1] had already observed, that ammonium sulfate decomposes without melting, and that it is the acid sulfate NH_4HSO_4 which melts at 140°. This is not greatly different from the melting point of potassium hydrogen sulfate, so that the low melting point is not inconsistent with the octet theory. The fused ammonium hydrogen sulfate is a very good electrolytic conductor and probably consists wholly of ions of NH_4^+ and HSO_4^-.

The relatively low melting point ammonium nitrate and the infusibility of the sulfate thus support the conclusion from the octet theory that the nitrate ion has a double bond, while in the sulfate ion the 4 oxygen atoms are held to the sulfur by single bonds. The ordinary valence theory on the other hand is not capable of showing such a distinction, for it gives double bonds for both anions.

Ammonium formate, NH_4CHO_2, melts at 115°, and at 180° decomposes into formamide and water. Although this melting point is not greatly below

[1] *Monatsh.* **23**, 1033 (1902).

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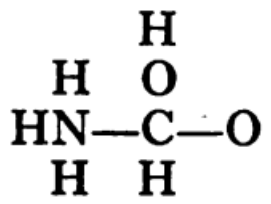
that of the potassium salt (150°) it is possible that the melt contains a proportion of molecules having the structure



in which one of the oxygen atoms is unicovalent. It is apparent that water can be readily split off from this molecule yielding formamide, H_2NCHO.

Schlenk and Holtz[1] have prepared a compound, triphenylmethyltetramethyl ammonium, in which 5 hydrocarbon residues are supposed to be attached to a single nitrogen atom, and which would thus furnish direct evidence of quinquevalent nitrogen. The compound is described as forming a "red shimmering crystalline mass with blue metallic luster," which is immediately decomposed by water yielding triphenylmethane and tetramethyl ammonium hydroxide. It is formed by the action of triphenylmethyl sodium on dry tetramethyl ammonium chloride in solution in ether.

Applying the octet theory to triphenylmethyl sodium by placing $e = 26$, $n = 4$, we find $p = 3$. Each of the 3 phenyl radicals shares a pair of electrons with the carbon atom, but the sodium atom shares no electrons with the organic radical. The constitution is, therefore,

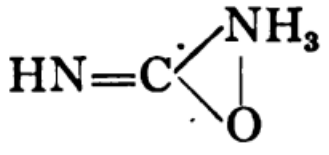
$$Na^+(CPh_3)^-.$$

The central carbon atom has a covalence of 3, but has its complete octet. This formula is in full accord with the unusual properties of this substance and explains, for example, its strong color and its reaction with ammonia to form triphenylmethane and sodium amide, $Na^+NH_2^-$. It is thus evident that the triphenylmethyltetramethyl ammonium which is derived from the triphenylmethyl sodium should have the constitution

$$[N(CH_3)_4]^+[CPh_3)]^-.$$

This substance should thus be a salt whose ions are held together by electrostatic attraction. The covalence of the nitrogen is 4 while that of the central carbon atom in the anion is 3. It is stated by Schlenk and Holtz that a solution of this substance in pyridine conducts the electric current, so there can be no question of its salt-like character.

The structure



[1] *Ber.* **49**, 603 (1916).

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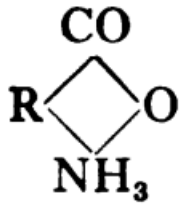
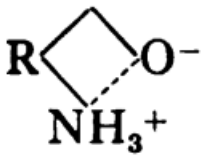
has been proposed for carbamide by E. A. Werner,[1] while W. A. Noyes and R. S. Potter,[2] in accordance with the views of others, have assumed the formula (*a*)



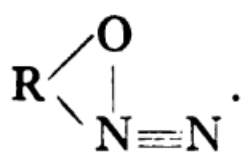
for certain amino acids. In the case of compounds of this second type the octet theory gives $p = 5$ which makes it impossible to place a covalence bond between the oxygen and the nitrogen. However, the formula may be written: (*b*)



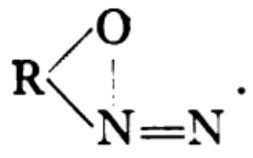
in which it is evident that the normally electrically neutral ammonia must become positively charged when it shares a pair of electrons with the carbon atom of the R group. Similarly the oxygen atom must be negatively charged because it has lost the positive charge which the NH_2 group has acquired (in being converted to NH_3). Under these conditions, in the absence of an ionizing solvent, it is natural that the positive and negative groups should be held together electrostatically as indicated by the dotted line in Formula *b*. This formula thus represents clearly the properties of the compound and is fully in accord with the experimental results of Noyes and Potter. Since in this case the oxygen and nitrogen cannot hold a pair of electrons in common, it seems desirable not to connect them by a valence bond in the formula.

Similar considerations apply to the structure of carbamide.

It is interesting that in the analogous case of the so-called diazophenols studied by Klemenc[3] the octet theory indicates the possibility of a true ring formula closed by covalence bonds. Klemenc has given evidence for the formula



The octet theory gives $p = 5$, which leads to the modification



The covalence of one of the nitrogen atoms is 4, while that of the other is two, but there is no development of free charges as in the case of the amino acids.

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[1] *Chem. Soc. Trans.* **107**, 715 (1915).
[2] *J. Am. Chem. Soc.* **37**, 189 (1915)
[3] *Ber.* **47**, 1407 (1914).

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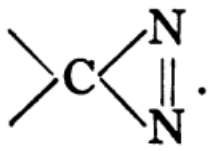
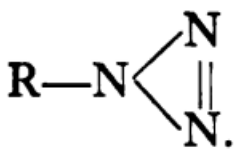
The formula given for diphenylene-diazomethane, $(C_6H_4)_2C{=}N{\equiv}N$,[1] is consistent with the octet theory if the triple bond is replaced by a double bond. In general, it is, perhaps, probable that $>C{=}N{=}N$ represents the diazo group rather than



The diazonium compounds may have either the structure $(R{-}N{\equiv}N)^+ OH^-$ or $R{-}N{=}N{-}OH$. This tautomerism explains the fact that in some cases these compounds exhibit acid as well as alkaline properties, while the unusual triple bond explains the explosive properties. The positive charge is probably not localized on either nitrogen atom but the $-N{=}N$ group as a whole is positive because it shares its electrons with the R group.

The triazo compounds RN_3 may have the structure $R{-}N{=}N{=}N$ rather than



Hydronitric acid is then $H{-}N{=}N{=}N$ and the nitride ion has the very symmetrical structure $N{=}N{=}N$. This structure is in full accord with the experimental facts referred to by Turrentine[2] in his discussion of the structure of hydronitric acid, from which he concludes that the structure should be $H{-}N{=}N{=}N$.

The properties of hydroxylamine indicate that this substance exists in two tautomeric forms[3] which may be represented according to the octet theory by (I) $H_2N{-}OH$; and (II) $H_3N{-}O$; the second of these formulas corresponding to that of the amine oxides already considered. The relationship of this compound to hydrogen peroxide discussed by L. W. Jones is thus made particularly clear, for this latter substance also exists in two tautometic forms.

(I) $H{-}O{-}O{-}H$ and (II) $H_2O{-}O$.

The form II contains in both cases unicovalent oxygen atoms and these formulas thus account directly for the oxidizing properties of these substances.

Hydrogen ions (or nuclei) are able to attach themselves to the free pair of electrons of the nitrogen octet in H_2NOH to form an ion H_3NOH^+. But the tendency to form this ion is weaker than that by which the ammonium ion is formed from ammonia and the hydrogen ion because the larger charge on the nucleus of the oxygen atom displaces the electrons of the nitrogen octet towards the oxygen atom, while the nucleus of the nitrogen atom is

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[1] Staudinger and Gaule, *Ber.* **49**, 1961 (1916).

[2] *J. Am. Chem. Soc.* **36**, 23 (1914).

[3] L. W. Jones, *J. Am. Chem. Soc.* **36**, 1268 (1914).

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displaced in the opposite direction. The presence of the hydroxyl group thus causes a decrease in the force with which the octet of the nitrogen atom holds hydrogen nuclei. There is no necessity for assuming polar valence.

For these reasons hydroxylamine has much weaker basic properties than ammonia. Notwithstanding this, the salts of hydroxylamine such as NH_3OHCl are completely ionized whether in solution or in the solid state. The reason that ammonia in acqueous solution is a weak base as compared to potassium hydroxide is that only a small fraction of the ammonia molecules combines with hydrogen ions from the water forming ammonium ions and thus liberating hydroxyl ions. The weakness of ammonia as a base is not to be looked upon as due to a lack of ionization of ammonium hydroxide, for this substance, according to the octet theory, can only exist in the completely ionized condition.

Acids, Bases and Salts

We have just seen why such substances as ammonia, hydroxylamine, etc., behave as weak bases. The octet theory indicates, however, that potassium hydroxide, barium hydroxide, and tetramethyl ammonium hydroxide can exist only in the ionized condition. That is, even in the solid state, potassium hydroxide consists of potassium ions and hydroxyl ions held together by their electrostatic attraction. In tetramethylammonium hydroxide, the 4 methyl groups share all four pairs of electrons of the nitrogen octet, so that there are no pairs of electrons by which the oxygen could be held. Here again the substance is completely ionized. It follows, therefore, directly that this substance must be as strong a base as potassium hydroxide. For the same reason the compounds $P(CH_3)_4OH$ and $S(CH_3)_3OH$ are strong bases.

In the hydrochloric acid molecule the hydrogen nucleus shares a pair of electrons with the chlorine atom. Anhydrous liquid hydrogen chloride is, therefore, a non-conductor of electricity since there are no free ions. But when this substance is brought into contact with water, the hydrogen nuclei can attach themselves more easily to the unshared pairs of electrons in the octets of the water molecules than to the chlorine atoms, since the nuclei of the oxygen atoms have smaller positive charges than those of the chlorine atoms. The result is that the hydrogen nuclei become hydrated hydrogen ions, and the chlorine ions remain in solution. This explanation of the separation of the hydrochloric acid molecule into ions is not essentially different from that which attributes the effect to the high dielectric constant of the water.

If we consider another substance such as hydrogen sulfide, it is clear that the tendency for the hydrogen nuclei to separate from the octet to which they were originally attached may be very much less. The smaller positive charge on the kernel of the sulfur atom as compared with that of the

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chlorine atom causes the hydrogen nucleus to be much more firmly held. Another way of expressing this relationship is to say that chlorine readily assumes a form in which it has the covalence of zero, while sulfur has a greater tendency to be dicovalent than unicovalent. Ammonia, as we have seen, acts as a base rather than as an acid. That it thus tends to take up a fourth hydrogen nucleus instead of giving up those that it has, is due to the smaller positive charge on its kernel, and to the fact that the 4 nuclei enable it to assume a particularly stable form.

For these same reasons methane acts neither as an acid nor as a base. The small charge on the kernel allows the 4 hydrogen nuclei to be very firmly held by the 4 pairs of electrons so that acid properties are absent. There can be no basic properties because the molecule cannot take up any more hydrogen nuclei, all 4 pairs of electrons in the octet already being occupied.

From this viewpoint, acids are substances from whose molecules hydrogen nuclei are readily detached, while bases are substances whose molecules can easily take up hydrogen nuclei. The more easily the hydrogen nuclei are given up, the stronger the acid which results: the greater the tendency to take up hydrogen nuclei the stronger the base. Typical salts, on the other hand, are completely ionized even in the solid state, and are, of course, completely ionized in solution. The variation in electric conductivities, osmotic pressures, etc., of salt solutions is quantitatively explained by Milner and Ghosh as due to the constraints caused by the electric charges which tend to produce a uniform distribution of positive and negative ions, whereas if the particles were uncharged there would be a random distribution.

There are certain substances usually regarded as salts, whose aqueous solutions show relatively little conductivity. Mercuric chloride and cyanide, cadmium iodide, etc., are typical examples of this kind. Mercuric and cadmium ions unquestionably have strong external fields of force in addition to the forces caused by their electric charges. According to the theory developed in a previous paper the ions of calcium and strontium differ from atoms of argon and krypton only in their electric charges. Since the stray forces around the atoms of the inert gases are very small, it follows then that the properties of the ions of calcium, strontium, etc., are determined almost wholly by the charges on the ions. But cadmium and mercuric ions have structures like atoms of palladium and platinum, respectively, so that, as in these latter atoms, it must be assumed that there are strong fields of force around the ions in addition to those caused by their charges. It is, therefore, probable that in mercuric chloride, the atoms exist as ions, but that these ions do not separate from each other when the substance goes into solution. The existence of the various organic compounds and complex ions of mercury furnishes abundant confirmation of this theory of strong secondary valence forces about atoms of mercury and other related elements.

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Isomerism of Cyanates, Cyanides, Nitrides, Etc.

It is well known that organic cyanates, cyanides and nitrites, exist in two isomeric forms. According to the octet theory the constitutions of these substances are as follows:

	p	Normal	Iso
Cyanates	5	R - O=C=N or R—O—C≡N	R—N=C=O
Cyanides or nitriles	4	R—C≡N	R—(NC)
Nitrites or nitro-compounds	4	R—O—N=0	

The second column gives p the number of pairs of electrons held in common between the atoms as calculated from the octet equation.

In the isonitriles the nitrogen and carbon kernels are probably contained within a single octet as in the cyanogen ion, and in the nitrogen and carbon monoxide molecules.

If we apply the octet theory to the structure of inorganic cyanates, cyanides and nitrites we find the following constitutions:

Cyanates, $p = 4$,	$K^+[O=C=N]^-$
Cyanides,	$K^+[CN]^-$
Nitrites, $p = 3$,	$K^+[O—N=O]^-$

The theory thus indicates that these substances differ essentially from the corresponding organic compounds in that the atoms of the metal are not attached to definite atoms of the acid radical. It is, therefore, evident from the octet theory that these substances should not exist in two isomeric modifications, and that the structures of these inorganic compounds do not correspond to either the normal or to the iso organic derivations. These conclusions are in full accord with the facts.

Free cyanic, hydrocyanic and nitrous acids exist in only one form each, although we cannot assume that these exist like their salts, in the completely ionized condition. These facts simply illustrate again the mobility of the hydrogen nucleus when bound by atoms having a covalence less than 4. We may, therefore, consider that in these free acids both the modifications observed among the organic derivatives exist together in tautomeric equilibrium.

Phosphonium, Arsonium, Sulfonium and Oxonium Compounds

Whereas the ammonia molecule has a relatively strong tendency to take up a hydrogen nucleus to form the ammonium ion, the corresponding tendency of phosphine to take up the hydrogen nucleus is very weak. This decrease in the affinity for hydrogen nuclei in passing from nitrogen to phos-

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phorus, corresponds to the fact that hydrochloric acid is a stronger acid than hydrofluoric and hydrogen sulfide has stronger acid properties than water.

The introduction of a chlorine atom into acetic acid to form chloroacetic acid, according to the viewpoint of G. N. Lewis, displaces all the electrons towards the chlorine atom. This decreases the forces holding the hydrogen nucleus in the hydroxyl group and by allowing this hydrogen ion to be more readily detached, makes the chloroacetic acid a stronger acid than acetic. A replacement of the same hydrogen atoms by alkyl radicals allows the electrons to shift towards the hydroxyl group, increasing the forces holding the hydrogen nucleus and making the acid weaker. In a similar way the replacement of the hydrogen atoms in phosphine increases the tendency for the molecule to take up hydrogen nuclei and strengthens the basic properties. Thus trimethyl-phosphine has distinctly basic properties, although these are much less than those of trimethylamine.

On the other hand the phosphonium bases or quaternary compounds such as tetramethyl-phosphonium hydroxide are exceedingly strong bases quite comparable with potassium hydroxide and tetramethyl-ammonium hydroxide. In these compounds, just as in ordinary ammonium salts the central atom must be quadricovalent and the negative radical thus exists as an ion which does not share electrons with the positive radical.

The basic properties of the arseine derivatives are less marked. Thus even tertiary arsines do not have basic properties. On the other hand, as is to be expected, the quaternary arsonium bases are about as strongly basic as potassium hydroxide and the other quaternary bases.

As distinguished from the corresponding ammonium compounds, it is possible to replace the hydrogen of alkyl substituted phosphines and especially arsines by chlorine. All such compounds whose formulas can be written by giving arsenic a valence of 3 are of course in agreement with the octet theory. The structures of the various chlorine addition compounds, should however, be as follows:

$$[(CH_3)AsCl_3]^+Cl^-$$

$$[(CH_3)_2AsCl_2]^+Cl^-$$

$$[(CH_3)_3AsCl]^+Cl^-$$

$$[As(CH_3)_4]^+Cl^-$$

In the corresponding oxides $(CH_3)AsO(OH)_2$, $(CH_3)_2AsO(OH)$ and $(CH_3)_3AsO$, all 4 radicals are attached directly to the quadricovalent arsenic atom, so that these compounds are not salt-like in character.

For sulfonium compounds such as $(CH_3)_3SI$ we place $e = 34$, $n = 5$ and find $p = 3$. The constitution is thus $[S(CH_3)_3]^+I^-$, where the sulfur atom is tercovalent. The corresponding base $[S(CH_3)_3]^+OH^-$ is, of course, completely ionized and is, therefore, comparable to potassium hydroxide.

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In compounds with oxygen and organic radicals, sulfur takes, with almost equal ease, covalences of 3 or 4. This leads to a great variety of organic compounds. The following table gives a list of such types of compounds together with the constitutions as derived from the octet theory:

Organic Sulfur-Oxygen Compounds, Etc.

	Quadricovalent sulfur		Tercovalent sulfur
A. Sulfates	$(K^+)_2\left[\begin{matrix}O\\O\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]^{--}$	F. Sulfites	$(K^+)_2\left[O\!-\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]^{--}$
B. Sulfonates	$K^+\left[\begin{matrix}R\\O\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]^{-}$	G. Sulfinates	$K^+\left[R\!-\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]^{-}$
C. Sulfones	$\left[\begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]$	H. Dialkyl sulfoxides	$R\!-\!S\!<\!\begin{matrix}R\\O\end{matrix}$
D. Trialkyl sulfine iodide	$\left[\begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}R\\O\end{matrix}\right]^{+}I^-$	I. Sulfonium compounds	$\left[R\!-\!S\!<\!\begin{matrix}R\\R\end{matrix}\right]^{+}I^-$
E. Tetralkyl sulfonium iodide	$\left[\begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}R\\R\end{matrix}\right]^{++}(I^-)_2$		

In addition to these there are, of course, various possible esters of the acids, such, as

A. $\begin{matrix}RO\\RO\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}$ and $K^+\left[\begin{matrix}RO\\O\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]$

B. $\begin{matrix}R\\RO\end{matrix}\!>\!S\!<\!\begin{matrix}O\\O\end{matrix}$

F. $\begin{matrix}RO\\RO\end{matrix}\!>\!S\!-\!O$ and $K^+\left[RO\!-\!S\!<\!\begin{matrix}O\\O\end{matrix}\right]$

G. $R\!-\!O\!-\!S\!<\!\begin{matrix}R\\O\end{matrix}$

where the letters A, B, F and G refer to the corresponding substances in the preceding table.

The compounds given under E in the first table, namely, compounds of the type $[S(CH_3)_4]^{++}I_2^-$ have, I believe, not been isolated. But a closely corresponding cyclic compound trimethylene-dimethyl-sulfonium diodide $[CH_2.CH_2.CH_2.S(CH_3)_2]^{++}I_2^-$ has been prepared and studied by Grishkevich-Trokhimovskii.[1] He found that both iodine atoms are equally ionized and are precipitated by silver nitrate.

[1] *J. Russ. Phys. Chem. Soc.* **48**, 880 (1916).

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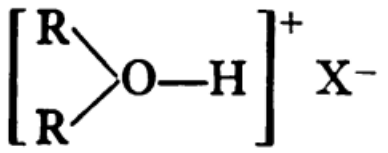
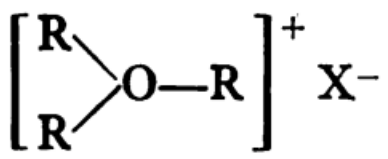
For oxonium compounds such as those of the type $R_2O.OX$ we place $e = 28$; $n = 4$ and find $p = 2$. The hydrogen nucleus can, however, attach itself to one of the unoccupied pairs of electrons of the oxygen atom so we arrive at the structure



For compounds of the $R_2O.RX$ type we place $e = 34$; $n = 5$ and find $p = 3$, whence the constitution is



corresponding exactly to the sulfonium compounds.

The constitutions of the phosphonium, sulfonium, oxonium, compounds, etc., arrived at by the octet theory correspond to those found by Werner's theory. The octet theory, however, has the advantage that it does not require special assumptions regarding valence for compounds of each of these types.

Summary

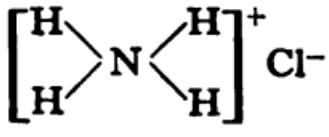
The octet theory of valence which has been described in previous papers is here applied particularly to organic nitrogen compounds, although the general application of the theory to inorganic nitrogen compounds and to salts is discussed.

The numbers of available electrons in the outside shell of any atom is usually given by the ordinal number of the column of the periodic table in which the element is found. This number, which we may represent by E, corresponds to the maximum positive valence of the ordinary valence theory and is one for sodium, 4 for carbon, 5 for nitrogen, 6 for oxygen, and 7 for chlorine.

It is readily proved that the octet theory is entirely in agreement with the ordinary valence theory whenever the ordinary formulas are based on valences of unity for hydrogen and $8-E$ for each other element. Thus the ordinary formulas agree with those of the octet theory whenever we take the following valences: hydrogen, one; carbon, 4; nitrogen and phosphorus, 3; oxygen and sulfur, 2; and chlorine, bromine, etc., one. On the other hand all formulas in which valences different from these have been used require modification according to the octet theory.

The octet theory is applied, among others, to the following compounds, whose formulas require modification.

Sodium chloride Na^+Cl^- (the covalence of both atoms is zero).

Ammonium chloride  (the nitrogen is quadricovalent).

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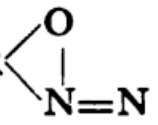
Triphenylmethyltetramethyl ammonium $[N(CH_3)_4]^+[CPh_3]^-$ (the nitrogen is quadricovalent while the central carbon atom in the anion is tercovalent).

Diazophenol 

Diazonium compounds $[R—N{\equiv}N]^+OH^-$ or $R—N{=}NOH$

Triazo-compounds $R—N{=}N{=}N$

Hydroxylamine H_2NOH or $H_3N—O$, etc.

According to this theory all salts are completely ionized even before they are brought into solution. This conclusion is, however, in accord with recent work of Milner, Ghosh and others. It explains why there are weak acids and weak bases but no weak salts.

The known cases of isomerism, including stereoisomerism, of nitrogen, phosphorus and sulfur compounds are in full accord with the octet theory.

The fact that organic cyanates, cyanides and nitrites exist in two isomeric forms, while the corresponding inorganic salts exist in only one form, is explained, since the nulcovalent atoms of the metals in the inorganic compounds are not attached to definite atoms of the acid radicals.

The available data on phosphonium, arsonium, sulfonium and oxonium compounds are in full accord with the octet theory, which gives for these ompounds constitutions closely resembling those previously given byc Werner.

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THE STRUCTURE OF ATOMS AND ITS BEARING ON CHEMICAL VALENCE

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ACCORDING to the well-established Rutherford-Bohr theory, all the positive electricity in an atom is concentrated in a *nucleus* at its center. The dimensions of this nucleus are negligibly small compared with those of the rest of the atom, its diameter being of the order of 0.00001 of that of the atom. The charge on the nucleus is an integral multiple of the charge of an electron but of course opposite in sign. The remainder of the atom consists of electrons arranged in space about the nucleus, the normal number of such electrons (called the *atomic number*) being equal to the number of unit positive charges on the nucleus, so that the atom as a whole is electrically neutral. If the number of electrons in the atom exceeds the atomic number we have a negatively charged atom or ion while in the reverse case a positively charged atom or ion results. The atomic number of any element has been found to be equal to the ordinal number of the element in the periodic table. Thus hydrogen has the atomic number one, helium 2, lithium 3, carbon 6, neon 10, chlorine 17, nickel 28, silver 47, cerium 58, tungsten 74, radium 88, and uranium 92. The atomic numbers can be determined experimentally from the X-ray spectrum so that we are not dependent upon the periodic table for our knowledge of these numbers.

Bohr, Sommerfeld, and others have developed an extensive and very successful theory of spectra upon the hypothesis that the electrons in atoms are in rapid rotation in plane orbits about the nucleus in much the same way as the planets revolve around the sun. Stark, Parson, and G. N. Lewis on the other hand, starting from chemical evidence, have assumed that the electrons are stationary in position. It should be noted that Bohr's theory has had its greatest success when applied to atoms or ions containing only one electron and that it seems incapable of explaining the chemical or ordinary physical properties of even such simple elements as lithium, carbon, or neon.

The two theories can, however, be reconciled if we consider that the electrons, as a result of forces which they exert on one another, rotate

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[EDITOR'S NOTE: The paper published in *J. Franklin Inst.* **187** (1919) was omitted to avoid repetition.]

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about certain definite positions in the atom which are distributed symmetrically in three dimensions. Thus for atoms containing only a single electron the chemical theory is in agreement with Bohr's theory. But for an atom such as neon the eight electrons in the outside layer would revolve around positions which are located about the nucleus in the same way that the eight corners of a cube are arranged about the center of the cube. This structure is not inconsistent with those parts of Bohr's theory which have received experimental confirmation. In fact, Born and Landé,[1] starting from Bohr's theory and without knowledge of Lewis' work, arrived at exactly this conception of the structure of atoms (i.e., the cubic atom) from a study of the compressibility of the salts of the alkali metals.

The atomic numbers and the properties of the inert gases furnish us with a clue to the arrangement of the electrons within atoms. The low boiling point, the high ionizing potential, the chemical inertness, etc., of helium prove that the arrangement of the electrons in the helium atom is more stable than that in any other atom. Since this atom contains two electrons we must conclude that a pair of electrons in the presence of a nucleus represents a very stable group. It is reasonable that with elements of higher atomic number there should be an even greater tendency for this stable pair of electrons to form about the nucleus. There are two sets of facts which furnish conclusive experimental evidence that this stable pair exists in all atoms above helium.

In the first place, the properties of lithium, beryllium, etc., show that in these elements also the first two electrons are held firmly while the remainder are easily detached. Thus, lithium readily forms a univalent positive ion by the detachment of one of the three electrons in its neutral atom. The divalence and other properties of beryllium prove that there is little or no tendency for a second stable pair of electrons to surround the first pair.

In the second place, the absence of irregularities in the observed K and L series of the X-ray spectra of the various elements proves that there are no sudden changes in the number of electrons in the innermost layers of electrons about the nucleus. From these two sets of facts, as well as from other evidence, we may take it as a fundamental principle that the arrangement of the inner electrons undergoes no change as we pass from elements of smaller to those of higher atomic number.

The properties of neon indicate that its atoms are more stable than those of any other element except helium. Since the atomic number is 10, and the first 2 electrons from a stable pair about the nucleus as in the helium atom, it follows directly that the other eight electrons arrange themselves in a second layer or shell possessing a very high stability. If these 8 electrons revolved about the nucleus in a single circular orbit or ring, as would be suggested

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[1] *Verh. d. phys. Ges.* **20**, 210 (1918).

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by Bohr's theory, there is no apparent reason why there should be any very great difference in stability between rings having 7, 8, or 9 electrons. On the other hand, we readily see that the geometrical symmetry of the arrangement of the 8 electrons at (or rotating about) the 8 corners of a cube would not only account for a high degree of stability but for the fact that at an arrangement of 7 or 9 electrons would have no such stability. Chemical considerations and Born and Landé's work on compressibility also lead us to this spatial arrangement of the electrons We shall refer to the stable group of 8 electrons by the term *octet*. From the principles already enunciated it is clear that in the atoms of all the elements above neon the inner electrons are arranged in the same way as those of neon.

From the atomic numbers of the inert gases we are thus able to determine the number of electrons in the various layers or shells of electrons which exist in the atoms. The results are summarized in Table I.

TABLE I

Distribution of Electrons in the Various Shells

Shell	Number of Electrons	Inert Gas Corresponding to Completed Layer
1st shell	$2 = 2\times1^2$	He 2
2nd shell, 1st layer	$8 = 2\times2^2$	Ne 10
2nd shell, 2nd layer	$8 = 2\times2^2$	Ar 18
3rd shell, 1st layer	$18 = 2\times3^2$	Kr 36
3rd shell, 2nd layer	$18 = 2\times3^2$	Xe 54
4th shell, 1st layer	$32 = 2\times4^2$	Nt 86

Thus the xenon atom with an atomic number 54 contains 54 electrons arranged as follows: Close to the nucleus are two electrons which constitute the first shell. This is surrounded by the second shell which contains two "layers" of 8 electrons each. The third shell, which in the xenon atom is the outside shell, contains 18 electrons.

An examination of the numbers of electrons in the layers (Table I, 2nd column) shows that they bear a simple mathematical relation to each other, namely, that they are proportional to the squares of the successive integers 1, 2, 3, and 4. This is be looked upon as perhaps the most fundamental fact underlying the periodic arrangement of the elements. It is significant that in Bohr's theory these same numbers, 1, 4, 9, 16, etc., play a prominent part. Thus the energies of the electron in the various "stationary states" are proportional to 1, $\frac{1}{4}$, $\frac{1}{9}$, $\frac{1}{16}$, etc., and the diameters of the various possible orbits in Bohr's theory are proportional to 1, 4, 9, 16, etc. In Bohr's theory the various stationary states correspond to different number of quanta (Planck's quantum theory), the innermost orbit corresponding to one quantum, the

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second orbit to two quanta, etc. We should thus consider (Table I) that the electrons in the 1st shell are monoquantic, those in both layers of the 2nd shell are diquantic, etc. It is interesting that Born and Landé from quite other evidence have concluded that the outermost electrons of the chlorine atom (2nd layer of the 2nd shell) are diquantic instead of triquantic as was at first assumed.

The foregoing theory of the arrangement of electrons in atoms explains the general features of the entire periodic system of the elements and is particularly successful in accounting for the position and the properties of the so-called 8th group and the rare earth elements. It also serves to correlate the magnetic properties of the elements.

Let us now consider the bearing of this theory of atomic structure on the phenomena of chemical valence. The outstanding feature of the theory is that there are certain groups of electrons, such as the pair in the first shell and the octet in the second, that have a remarkable stability. Those atoms in which all the electrons form parts of such stable groups (viz., the inert gases) will have no tendency to change the arrangement of their electrons and will thus not undergo chemical change. Suppose, however, we bring together an atom of fluorine (N = 9)[1] and an atom of sodium (N = 11). Ten electrons are needed for the stable pair in the first shell and the octet in the second shell, as in the neon atom. The sodium atom has one more electron than is needed to give this stable structure while the fluorine atom has one electron too few. It is obvious then that the extra electron of the sodium atom should pass over *completely* to the fluorine atom. This leaves the sodium atom with a single positive charge while the fluorine becomes negatively charged. If the two charged atoms or ions[2] were alone in space they would be drawn together by the electrostatic force and would move as a unit and thus constitute a molecule. However, if other sodium and fluorine ions are brought into contact with the "molecule" they will be attracted as well as the first one was. There will result (at not too high temperature) a space lattice consisting of alternate positive and negative ions and the "molecule" of sodium fluorine will have disappeared. Now this is just the structure which we find experimentally for sodium fluoride by Bragg's method of X-ray crystal analysis. There are no bonds linking individual pairs of atoms together. The salt is an electrolytic conductor only in so far as its ions are free to

[1] We will denote the atomic number of an element by N.

[2] It is convenient and it has been customary with many physicists to speak of a charged atom or molecule as an ion, irrespective of whether or not the particle is able to wander under the influence of an electric field. The writer has used the term in this way in his recent publications. This practice is very distasteful to many physical chemists and is apt to be misunderstood by them. Nevertheless, it seems to me probable, especially in view of the recent work of Milner and Ghosh, that it will be desirable to abandon the physical chemists' definition of the ion and to apply it to all charged atoms or molecules. The ion which wanders may then be referred to as a "free ion".

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move. In the molten condition or when dissolved in water, therefore, it becomes a good conductor.

The case of magnesium (N = 12) and oxygen (N = 8) is similar except that two electrons are transferred from the magnesium to the oxygen atom. The resulting ions have their electrons arranged exactly like those of the neon atoms and the ions of sodium and fluorine. Therefore, the crystalline form of magnesium oxide and sodium fluoride should be identical, and this prediction of the theory has been confirmed experimentally by Dr. A. W. Hull by the X-ray method. Because of the much greater forces acting between the ions as a result of the double charges, the stability of the magnesium oxide is much higher than that of the sodium fluoride. This is manifested by the high melting point, low conductivity, low solubility, and hardness of magnesium oxide.

Phosphorus (N = 15) and sulfur (N = 16) have, respectively, 5 and 6 electrons more than neon, and are thus capable of giving up these numbers of electrons. If these elements are brought into contact with an excess of fluorine (which because of its proximity to neon has a particularly strong tendency to take electrons) all the extra electrons pass to fluorine atoms. Thus a sulfur atom will supply electrons to 6 fluorine atoms and will form the compound SF_6. The force acting between the fluorine ions and the central sulfur ion is still electrostatic in nature but it must be nearly 6 times greater than the force between sodium and fluorine ions. Furthermore, the 6 fluorine ions would surround the sulfur ion so that there would be little stray field of force. Therefore, we should not expect sulfur fluoride to be salt-like in character but to consist of very stable molecules having weak external fields of force and, therefore, readily existing in the form of a gas. As a matter of fact this extraordinary substance has these properties developed to such a degree that it is an *odorless* and *tasteless* gas with a boiling point of −62°. Phosphorus pentafluoride, as would be expected from its less symmetrical structure, is a gas having greater chemical activity.

The fluosilicate ion SiF_6^{--} has a structure exactly like that of the sulfur fluoride molecule since the number and arrangement of the electrons are the same. This is clear if we consider that the atomic number of silicon is 14 while that of sulfur is 16. Thus if we should replace the nucleus of the sulfur atom in a molecule of sulfur fluoride by the nucleus of a silicon atom, without disturbing any of the surrounding electrons, we would have removed two positive charges and would obtain a negative ion with two negative charges of the formula SiF_6^{--}. In the presence of potassium ions we would then have the familiar salt potassium fluosilicate. The theory is thus capable of explaining typical complex salts. In fact, it is applicable to the whole field of inorganic compounds covered by the work of Werner, and helps to simplify the theory of such compounds. There is no time, however, to go into this subject.

The simple theory of atomic structure which we have discussed thus far explains perfectly what has usually been called "the maximum positive and

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negative valence". The maximum positive valence represents the number of electrons which the atom possesses in excess of the number needed to form one of the particularly stable configurations of electrons. On the other hand, the maximum negative valence is the number of electrons which the atom must take up in order to reach one of these stable configurations.

For example, magnesium has a positive valence of two, since its atomic number is 12 while that of neon is 10. Sulfur has a positive valence of 6 since it has 6 electrons more than neon; but it has a negative valence of two because it must take up two more electrons before it can assume a form like that of the argon atom.

It is clear, however, that this theory of valence is not yet complete.[1] It is not applicable to those cases where we have usually taken valences of 4 for sulfur, or 3 and 5 for chlorine, etc. But more especially it does not explain the structure of organic compounds and such substances as H_2, Cl_2, O_2, N_2H_4, PCl_3, etc.

J. J. Thomson, Stark, Bohr, and others had suggested that pairs of electrons held in common by two adjacent atoms may function in some cases as chemical bonds between the atoms, but this idea had not been combined with the conception of the stable groups of electrons or octets. G. N. Lewis, in an important paper in 1916, advanced the idea that the stable configurations of electrons in atom could share *pairs* of electrons with each other and he identified these pairs of electrons with the chemical bond of organic chemistry. This work of Lewis has been the basis and the inspiration of my work on valence and atomic structure.

As result of the sharing of electrons between octets, the number of octets that can be formed from a given number of electrons in increased. For example, two fluorine atoms, each having seven electrons in its outside shell, would not be able to form octets at all except by sharing electrons. By sharing a single pair of electrons, however, two octets can be formed since two octets holding a pair in common require only 14 electrons. This is clear if we consider two cubes with electrons at each of the eight corners. When the cubes are placed so that an edge of one is in contact with an edge of the other a single pair of electrons at the ends of the common edge will take the place of four electrons in the original cubes. For each pair of electrons held in common between two octets there is a decrease of two in the total number of electrons needed to form the octets.

Let e represent the number of electrons in the outside shell of the atoms that combine to form a molecule. Let n be the number of octets that are formed from these e electrons, and let p be the number of pairs of electrons which the

[1] The theories of Kossel, Lacomblé, Teudt, etc., which have recently been proposed in Germany, have not advanced beyond this point and are therefore very unsatisfactory as a general theory of valence.

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octets share with one another. Since every pair of electrons thus shared reduces by two the number of electrons required to form the molecule it follows that $e = 8n-2p$ or

$$p = \tfrac{1}{2}(8n-e).$$

This simple equation tells us in each case how many pairs of electrons or chemical bonds must exist in any given molecule *between the octets formed.* Hydrogen nuclei, however, may attach themselves to pairs of electrons in the octets which are not already shared. For example, in the formation of hydrogen fluoride from a hydrogen atom and a fluorine atom there are 8 electrons in the shells ($e = 8$). We place $n-1$ in the above equation and find $p = 0$. In other words, the fluorine atoms do not share electrons with each other. The hydrogen nucleus having given up its electron to the fluorine atom attaches itself to one of the pairs of electrons of the fluorine octet, and thus forms a molecule having a relatively weak external field of force. As a result, hydrogen fluoride is a liquid of low boiling point instead of being salt-like in character.

The equation given above is applicable to all types of compounds. For example, if we apply it to substances such as sodium fluoride, sulfur fluoride, or potassium fluosilicate, which were previously considered, we find in each case $p = 0$. In other words, there are no pairs of electrons holding the atoms of these compounds together. On the other hand if we consider the compound N_2H_4, we find $p = 1$. Since there are only two octets the pair of electrons must be between the two nitrogen atoms while the hydrogen nuclei attach themselves to pairs of electrons of the nitrogen octets. It can be readily shown that this simple theory is in fact identical with the accepted valence theory of organic chemistry and leads to the same structural formulas as the ordinary theory in all those cases where we can take the valence of nitrogen to be 3, oxygen and sulfur 2, chlorine and hydrogen one. In other cases such as those where quinquivalent nitrogen has been assumed, the new theory gives results different from the old but in each case in better agreement with the facts.

The theory indicates a series of new relationships between certain types of substances which I have termed *isosteric* substances. For example, it indicates that the molecules of carbon dioxide and nitrous oxide should have nearly identical structures and this is borne out by the extraordinary similarity in the physical properties of these gases. Nitrogen and carbon monoxide constitute another pair of gases which are similarly related. The same theory also points out a number of previously unsuspected cases of similarity of crystalline form (isomorphism).

It is clear that in the past the term valence has been used to cover what we may now recognize as three different types of valence, as follows:

1. Positive valence: the number of electrons an atom can give up.
2. Negative valence: the number of electrons an atom can take up.
3. Covalence: the number of pairs of electrons which an atom can share with its neighbors.

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It is recommended that only for valences of the covalence type should definite bonds be indicated in chemical formulas. One of the particular advantages of the present theory is that it becomes easy to distinguish between covalence and the other types and thus to predict with certainty in what way electrolytic dissociation will occur if at all.

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THE CHARGE ON THE ELECTRON AND THE VALUE OF PLANCK'S CONSTANT h*

Journal of the Franklin Institute
Vol. CLXXXIX, 603 (1920).

LEWIS AND ADAMS (*Phys. Rev.* (2), **3**, 92 (1914)) from a theory of ultimate rational units, i.e., by a kind of dimensional reasoning, have derived the following relation between Planck's constant h and the electron charge e.

$$h = \frac{e^2}{c} \times 32\pi^3 \sqrt[3]{\frac{\pi^2}{15}} \tag{1}$$

where c is the velocity of light (2.9986×10^{10} cm per sec). If we take for e the value 4.774×10^{-10} e.s. units as determined by Millikan (*Phys. Rev.* (2), **2**, 143 (1913)) this gives

$$h = 6.560 \times 10^{-27} \text{ erg seconds.}$$

In a recent paper R. T. Birge (*Phys. Rev.* **14**, 361 (1919)) has calculated h in seven different ways and obtains as the most probable value

$$h = 6.5543 \times 10^{-27}.$$

Every method of determining h, however, involves the use of e so that any error in this quantity produces a corresponding uncertainty in h. Sommerfeld in his recent book on atomic structure (*Atombau und Spectrallinien*, Nov., 1919) has given a new relation between h and e in terms of the Rydberg constants obtained with hydrogen and helium. From Bohr's theory, taking into account the masses of the nuclei of the atoms, and by comparing the spectra of hydrogen and helium, he is able to calculate the value of e/m with very great accuracy (here m is the mass of the electron). He obtains

$$e/m = 1.7686 \times 10^7 \text{ e.m. units,}$$
$$\text{or } c \times 1.7686 \times 10^7 \text{ e.s. units.}$$

Besides being based upon the spectroscopic wave lengths, this value involves a knowledge of the ratio of the atomic weights of helium and hydrogen (4.000 : 1.008). The relative error in e/m, however, is only about one-third as great as that in the ratio of the atomic weights. Sommerfeld has furthermore derived the relations

$$e = \frac{\alpha^3 c^2}{4\pi N_\infty (e/m)} \tag{2}$$

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where

$$\alpha = \frac{2\pi e^2}{hc} \tag{3}$$

Here N_∞ is the wave number corresponding to the Rydberg constant for an infinitely heavy nucleus. It has the value

$$N_\infty = 109737.11 \text{ cm}^{-1} \tag{4}$$

These equations together with the Lewis and Adams relation enable us to calculate a new value of the electron charge e. Combining Equations 1 and 3 we find

$$\alpha = \frac{1}{16\pi^2}\sqrt[3]{\frac{\pi^2}{15}} = 0.0072798 \tag{5}$$

Substituting this together with the values of $N\infty$ and e/m in Equation (2) gives

$$e = 4.745 \times 10^{-10} \text{ e.s. units} \tag{6}$$

while this value substituted in (1) gives

$$h = 6.481 \times 10^{-27} \text{ erg seconds.}$$

This value of e is about 0.6 per cent lower than that given by Millikan, who estimates the accuracy of his result as 0.2 per cent. However, Millikan's determination has never been checked by any independent method of comparable accuracy, so it seems possible that a constant error of the above magnitude might have affected his results. The value of h given by Equation (7) is 1.2 per cent lower than the value calculated by Birge but this results merely from the different value for e. The following table gives the values of h calculated from the seven sets of data used by Birge: first, using Millikan's value $e = 4.774$; and second, using the value $e = 4.745$.

Determinations of h

Method	Dependence on e	$e = 4.774$	$e = 4.745$
Stefan-Boltzmann Constant	$e4/3$	6.551	6.497
Wien Constant c_2	e	6.557	6.517
Bohr-Sommerfeld theory, Equations (2) and (3)	$e5/3$	6.548	6.481
Einstein's photo-electric equation	e	6.578	6.538
Quantum relation for X-rays	$e4/3$	6.555	6.501
Lewis and Adams theory	e^3	6.560	6.481
Quantum relation for ionization potentials . . .	e	6.579	6.539
	Average	6.555	6.507

The values of h calculated from $e = 4.745$ are consistently smaller than those based on Millikan's value, but they agree among themselves within the probable experimental error. In any case the results do not warrant the con-

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clusion that the Lewis and Adams or the Bohr-Sommerfeld theories are not rigorous. Unless one of these theories is incorrect or incomplete, however, the values of e and h represented by Equations (6) and (7) should have a much higher accuracy than any of the other experimental determinations given in the above table. Under these conditions it seems desirable that new determinations of the electron charge should be made, especially if new methods can be developed.

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THEORIES OF ATOMIC STRUCTURE

Nature
Vol. CV, 261 (1920).

IN A LETTER to *Nature* (March 11, p. 41) S. C. Bradford stated: "The great objection to Langmuir's theory of atomic structure is the difficulty of accepting his hypothesis of stationary electrons." The cases cited are all discussed in G. N. Lewis's paper, "The Atom and the Molecule" (*J. Am. Chem. Soc.* **38**, 762 (1916)), so it is scarcely fair to Lewis to refer to the theory as "Langmuir's theory".

Although Lewis frankly implied that the electrons in atoms are stationary, his theory of valency did not depend upon such an assumption. The chemical data give information in regard to the geometry of atoms, and, in particular, tell us of the kinds of symmetry which they possess. From the chemical point of view it is at present a matter of comparative indifference what the motions of the electrons may be so long as they conform to the required conditions of symmetry. For this reason I was careful to state in my first paper (*J. Franklin Inst.* **187**, 359 (1919), and *J. Am. Chem. Soc.* **41**, 932 (1919)) that "the electrons in atoms are either stationary *or rotate, revolve, or oscillate about definite positions in the atom.*" It was, perhaps, not sufficiently emphasised that the positions of the electrons shown in the diagrams may be regarded as the centres of their orbits.

It is sometimes thought that the success of Bohr's theory furnishes reason for believing that all the electrons in atoms are rotating in coplanar orbits about the nucleus. There is little justification for this opinion. The remarkable results yielded by Bohr's theory, particularly in the hands of Sommerfeld, for the case of the hydrogen atom and the helium ion seem to prove beyond question that in an atom containing only one electron this electron actually revolves in a circular or elliptical orbit about the nucleus. Although Bohr's theory has had some applications to other atoms, these are, for the most part, of a very general nature, such as those which relate to the combination principle. The theory does not give a satisfactory model even for such simple structures as the hydrogen molecule or helium atom (see, for example, Sommerfeld's recent book, *Atombau und Spectrallinien*).

From the chemical point of view Bohr's theory is wholly unsatisfactory when applied to atoms containing more than one electron. Thus, according to Bohr's calculations (*Phil. Mag.* **26**, 492 (1913)), a lithium nucleus sur-

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rounded by three equidistant electrons should have less potential energy (and, therefore, greater stability) than one in which one electron is further from the nucleus than the other two. Bohr's theory thus gives no reason for the contrast between the properties of lithium and helium.

The two theories are not mutually incompatible if we consider that, in general, the electrons do not revolve about the nucleus, but about definite positions symmetrically distributed in three dimensions with respect to the nucleus. It is interesting to note that Born and Landé (*Verh. deut. physik. Ges.* **20**, 210, 230 (1918)), starting out from Bohr's theory and without knowledge of Lewis's work, were led to the theory of the cubical atom by a study of the compressibilities of the alkali halides. They conclude that the electron orbits do not lie in a plane, but are arranged in space with cubic symmetry. Sommerfeld in his book suggests that this conception may help to solve some of the outstanding difficulties, and evidently does not consider it inconsistent with Bohr's theory.

In the case of atoms which do not share electrons with other atoms, it is logical to assume that each electron in the outer shell has its own orbit. Thus the atoms Ne, Na^+, Mg^{++}, F^-, and the S atom in SF_6 should have cubic symmetry, the eight outer electrons revolving about positions located at the corners of a cube. But where a pair of electrons is held in common between two atoms, the chemical evidence indicates that the pair acts as a unit. When an atom shares four pairs of electrons with its neighbors, it thus has tetrahedral rather than cubic symmetry. So far as the chemical evidence is concerned, it would be satisfactory to adopt Bohr's model for the hydrogen molecule to represent the pair of electrons which constitutes the chemical bond. We may thus picture the chemical bond as a pair of electrons revolving in a single orbit about the line connecting the centers of the two atoms.

Bohr in his 1913 paper (*Phil. Mag.* **26**, 874) states: "The configuration suggested by the theory for a molecule of CH_4 is of the ordinary tetrahedron type; the carbon nucleus surrounded by a very small ring of two electrons being situated in the center, and a hydrogen nucleus in every corner. The chemical bonds are represented by four rings of two electrons each rotating round the lines connecting the center and the corners." This structure is quite consistent with the octet theory. Bohr did not, in general, identify a pair of electrons with a valency bond.

When we consider, however, that Bohr's theory in its present form does not furnish an explanation of the stability of the pair of electrons in the helium atom and in the bond between atoms, it is evident that the model described above can scarcely be regarded as satisfactory. It seems as though some factor of vital importance is still missing in Bohr's theory. The chemical data suggest that the ultimate theory will be extremely simple, but perhaps more radical than anything yet proposed.

I am in full agreement with the views put forward by Dr. H. S. Allen in *Nature* for March 18, p. 71.

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THE STRUCTURE OF THE HELIUM ATOM

Science, N.S.
Vol. LI, No. 1329, 605, June (1920).

ACCORDING to the model which Bohr proposed in 1913, the helium atom consists of two electrons moving in a single circular orbit having the nucleus at its center. The electrons remain at the opposite ends of a diameter and thus rotate in the same direction about the nucleus. The angular momentum of each electron is assumed to be $h/2\pi$, where h is the quantum constant. The ionizing potential of helium calculated by this theory is 28.8 volts. Recent experimental determinations by Franck and Knipping have given 25.4 ± 0.25 volts. Bohr's theory is approximately right but does not give the true structure.

For the hydrogen atom and helium ion, atoms containing but a single electron, Bohr's theory seems to be rigorously correct. For atoms containing more than one electron there are many facts which indicate that modifications or extensions are needed.

The chemical properties of the elements, particularly the periodic relationships and the phenomena of valence, have shown definitely that the electrons are not in general arranged in coplanar orbits. According to the theory which I advanced last year, the electrons in their most stable arrangements move only within certain limited regions about the nucleus, each of these cells containing not more than two electrons. The atoms of the inert gases were found to have their cells arranged symmetrically with respect to an equatorial plane, no electrons however ever lying in this plane. According to this view, the two electrons in the helium atom should not move in the same orbit but in separate orbits symmetrically located with respect to the equatorial plane. The two electrons in the hydrogen molecule (and in every pair of electrons which acts as a chemical bond between atoms) must be related to one another in the same way as those of the helium atom.

The most obvious model of this type is one in which the two electrons move in two circular orbits in parallel planes equidistant from the nucleus. By properly choosing the diameters of the orbits, the force of repulsion between the electrons is compensated by the component of the attractive force of the nucleus perpendicular to the plane. This model however proves impossible as it gives a negative value (-5.8 volts) for the ionizing potential.

[EDITOR'S NOTE: A more detailed account of this paper was published in *Phys. Rev.* **17**, 339 (1921).]

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A. Landé[1] has recently proposed a model for the eight electrons of an octet in which each electron occupies a cell bounded by octants of a spherical surface. The eight electrons move in such a way that their positions are symmetrically placed with respect to three mutually perpendicular planes which pass through the nucleus. When one electron approaches one of these planes it is retarded by the repulsion of the electron on the other side of the plane and is thus prevented from passing through the plane. Although each electron remains within a given octant of the spherical region about the nucleus, yet the momentum of the electron is transferred to the electrons in adjacent cells across the cell boundaries. In this model the momentum travels continuously around the atom in a circular path, being relayed from electron to electron. Thus even though the electrons do not leave their respective cells, the mathematical equations for their motion are very closely related to those which apply to the motions of electrons in circular orbits about the nucleus. Landé's calculations lead to the conclusions that this type of motion is less stable than one in which all eight electrons move in a single plane orbit. This objection can be overcome if we assume that the angular momentum of each electron is $h/2\pi$ instead of the double value which is usually assumed for the electrons in the second shell. In fact, this conception gives grounds for believing that all electrons in their most stable positions in atoms, have orbits corresponding to single quanta and it is only because we have assumed coplanar orbits that we have been led to the conclusion that the outer orbits correspond to increasing numbers of quanta.

This model of Landé's has suggested to me that there should be a similar interrelationship between the two electrons of the helium atom, and also of the hydrogen molecule, and of the pair of electrons constituting the chemical bond.

I assume that the two electrons have no velocity components perpendicular to the plane which passes through the nucleus and the two electrons. The motion is thus confined to a single plane. The two electrons, however, are assumed to rotate about the nucleus in *opposite* directions, and in such a way they are always located symmetrically with respect to a line passing through the nucleus. Consider for example that this line of symmetry is horizontal and that one electron is located directly above the nucleus at a unit distance, and is moving horizontally to the right. Then the other electron will be located at an equal distance below the nucleus and will move in the same direction and with the same velocity. If there were no forces of repulsion between the two electrons, and if we choose the proper velocities, it is clear that the two electrons might move in a single circular orbit about the nucleus, but in opposite directions of rotation. This would require, however, that the electrons should pass through each other twice in each complete revolution. When we take into account the mutual repulsion of the electrons, we see that their initial velocities will suffice

[1] *Verh. deut. phys. Ges.* **21**, 653 (1919).

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to carry them only within a certain distance of each other, and they will then tend to return in the general direction from which they came. With properly chosen initial conditions the electrons will return back exactly on the paths in which they advanced and will then pass over (towards the left) to the other side of the nucleus and complete the second half of an oscillation. Each electron has its own orbit which never crosses the line of symmetry. The orbit however does not consist of a closed curve, but a curved line of finite length along which the electron oscillates.

Unfortunately the equations of motion for this three-body problem are difficult to handle and I have only been able to determine the motion by laborious numerical calculations involving a series of approximations. These however, can be carried to any desired degree of accuracy. By four approximations I have been able to calculate the path and the velocities, etc., to within about one tenth per cent. It is to be hoped that a general solution of this special type of three-body problem may be worked out, if indeed one is not already known to those more familar with this type of problem.

The results of this calculation show that the path of each electron is very nearly an arc of an eccentric circle, extending 77° 58′ each way from the mid-point (as measured from the nucleus). If we take the radius vector at the mid-point to be unity then the radius at the end of the arc is 1.138. The angular velocity of the electron at the mid-point of the path is such that if it continued with this velocity it would travel through 105° 23′ during the time that it actually takes to move to the end of its orbit (i.e., through 77° 58′).

By imposing the quantum condition that the angular momentum of each electron at the mid-point of its path shall be $h/2\pi$, it becomes possible to calculate the radius vector and the velocity in absolute units. The radius vector for the electron at its midpoint is 0.2534×10^{-8} cm which is 0.8359 of the radius of the orbit of Bohr's model (0.3031×10^{-8} cm). Even at the end of the orbit the radius (0.2882×10^{-8} cm) is less than that of the Bohr model. The angular velocity at the mid-point is 1.431 times that of electrons of the Bohr atom. The number of complete oscillations per second is 24.63×10^{15}, which is 1.222 times as great as the number of revolutions in the Bohr atom (20.16×10^{15} per second). The total energy (kinetic plus potential) of the oscillating atom is 0.9615 of that of the Bohr atom. The ionizing potential of helium according to the new model should be 25.59 volts which agrees with Franck and Knipping's experimental determination within the limits of error given by them, but differs from the 28.8 volts given by Bohr's theory by nearly ten times the experimental error.

The oscillating model is thus not only satisfactory from a chemical point of view but is in quantitative agreement with the properties of helium. The fact that there can be no corresponding structure with three electrons is in accord with the fact that lithium (which has three electrons) is an element having totally different properties from helium.

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The calculation for the hydrogen molecule involves greater difficulties. Bohr's model with the two electrons moving in a single circular orbit gives a heat of dissociation of about 63,000 calories, whereas experiment gives about 90,000. The calculations for helium have shown that the radius of the oscillating atom is considerably smaller than that of the Bohr atom, so that the force of attraction between the electrons and the nucleus is much (20 per cent or more) greater. In the hydrogen molecule this increased force may result in drawing the two nuclei closer together thus increasing the stability of the molecule. Calculations of the orbits of the electrons in the hydrogen molecule are in progress.

The final results with a description of the methods of calculation will be published probably in the *Physical Review* and the *Journal of the American Chemical Society*.

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THE STRUCTURE OF THE HELIUM ATOM[1]

Physical Review
Vol. XVII, No. 3, March (1921).

SYNOPSIS

Models for the Helium Atom.—(1) *Bohr's model* is unsatisfactory because it gives too great a value for the ionizing potential and is not in accord with the optical and magnetic properties of helium. Now the chemical evidence suggests that each electron in an atom has its own separate orbit, and that these orbits are closely interrelated. Accordingly two new models are considered. (2) In the *double circle-model* the two electrons are assumed to move in two separate, parallel, circular orbits. The model, however, is unstable, for the ionizing potential, computed by applying the quantum theory, comes out negative. Another objection is that the magnetic moment is not zero. (3) In the *semi-circular model* each electron is assumed to oscillate back and forth along an approximately semi-circular path in accord with classical mechanics, each being brought to rest at the end of its path by the repulsion of the other. Assuming the maximum angular momentum of each equal to $h/2\pi$, the absolute dimensions of the model were computed. The total energy comes out less than for the Bohr model, and the ionizing potential, 25.62 volts, agrees closely with the experimental value. The magnetic moment is zero.

Application of the Quantum Theory to Coupled Electrons.—The success of the semi-circular model in-giving the correct value for the ionizing potential of helium suggests that in the case of coupled electrons the quantum theory should be applied not to the momentum of the individual electrons according to relation $\int pdq = h/2\pi$, but rather to the momentum which, by being relayed from one electron to another, passes in each direction around the nucleus.

BOHR'S models for the hydrogen atom and the positively charged helium ion are now almost universally accepted. The extraordinary success with which even the fine structure of the lines of the hydrogen and helium spectra have been worked out from these models by Bohr, Sommerfeld and others, is convincing proof that in these cases the structure is definitely known. On the other hand Bohr's models for the helium atom,[2] and for all the molecules considered by him, although they have seemed satisfactory in many respects, have not given quantitative agreement with the spectra or other properties. For example the ionizing potential of helium according to Bohr's model should be 28.8 volts while experiment gives 25.4 ± 0.25 volts.[3] Sommerfeld[4] states that this model is not in agreement with the optical properties of helium. Similarly, the molecular heat of dissociation of hydrogen into atoms

[1] A preliminary notice giving some of the results of this paper was published in *Science*, *N.S.* **51**, 605 (1920).

[2] *Phil. Mag.* **26**, 488 (1913).

[3] Frank and Knipping, *Phys. Zeit.* **20**, 481 (1919).

[4] *Atombau*, 1st edition, p. 70, Braunschweig, 1919.

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should be 63,000 calories according to Bohr's model, while experiment gives about 84,000 calories.[1] From the behavior of the many-lined spectrum of hydrogen in a magnetic field Lenz[2] has concluded that the electrons in the hydrogen molecule can have no momentum about the axis of symmetry. In other words either each electron must have zero momentum, or the momenta of the two electrons must be equal and opposite.

From the chemical point of view Bohr's models are satisfactory only in the case of the hydrogen atom. Evidence was given by A. L. Parson[3] that in many atoms the electrons are arranged with cubic symmetry. G. N. Lewis[4] emphasized the importance of pairs of electrons and *octets* or groups of eight electrons. Kossel[5] showed that certain groupings of electrons in atoms, corresponding to the inert gases, are of unusual stability. These theories have been extended in a series of papers by the writer.[6] Similar conclusions regarding the structure and stability of the octet has been reached by M. Born[7] from evidence of an entirely different kind. Landé in a series of papers[8] has developed a mathematical theory of the motions of eight electrons about points in atoms distributed with cubic symmetry. Landé and Born, however, have not given consideration to the fact that the pairs of electrons in the helium atom and in the kernels of other atoms, exhibit a stability even greater than that of the octet.

Bohr's calculations,[9] based on coplanar, concentric, circular orbits gave no indications that a pair of electrons bound by a nucleus would show unusual stability. If $-W$ represents the total energy (kinetic plus potential) of an atom then the most stable model should be that which has the greatest value of W. For Bohr's model of the helium atom, in which the two electrons revolve about the nucleus in a single circular orbit, $W = 6.13W_0$, where W_0 is the value of W corresponding to the hydrogen atom. Bohr's model of the helium ion gives $W = 4W_0$. For a lithium atom, with the three electrons in a single circular ring, $W = 17.61W_0$, but if there are two electrons in an inner ring and a single electron in an outer ring $W = 16.02W_0$. For the lithium ion with two electrons in a single ring Bohr finds $W = 15.13W_0$. Therefore the work needed to remove an electron from a lithium atom (first model) is $2.48W_0$, while the work required to take an electron from a helium atom

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[1] Langmuir, *J. Am. Chem. Soc.* **37**, 417 (1915).

[2] *Verh. deut. physik. Ges.* **21**, 632 (1919).

[3] *Smithsonian Inst. Publ. Miscel. Collections* **65**, No. 11 (1915).

[4] *J. Am. Chem. Soc.* **38**, 762 (1916).

[5] *Ann. Physik* **49**, 229 (1916).

[6] Langmuir, *J. Franklin Inst.* **187**, 359 (1919); *J. Am. Chem. Soc.* **41**, 868, 1543 (1919); **42**, 274 (1920); *Phys. Rev., N.S.* **13**, 300 (1919); *Proc. Natl. Acad. Sci.* **5**, 252 (1919); *Nature*, April 29 (1920).

[7] *Verh. deut. physik. Ges.* **20**, 230 (1918).

[8] *Verh. deut. physik. Ges.* **21**, 2, 644, 653 (1919); *Zeit. f. Physik* **2**, 83, 380 (1920).

[9] *Phil. Mag.* **26**, 492 (1913).

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is only $2.13W_0$. It should thus be easier to ionize helium than lithium vapor. Bohr's theory is even less applicable to beryllium for the model with the greatest value of W is that in which all four electrons revolve in a single ring ($W = 37.04W_0$). Bohr's original theory would thus indicate that lithium and beryllium (and all subsequent elements) should be inert gases having even greater stability than helium.

The remarkable stability of the pair and the octet is not explainable on the basis of Bohr's theory. The chemical and physical properties of the elements prove that the electrons in atoms are coupled together in a rather complex manner, which seems quite inconsistent with the ordinary properties of the electron. I have tried to summarize the characteristics of this electron coupling in a series of postulates.[1] It is probable that an understanding of these postulates will require more definite knowledge of the mechanism underlying the quantum theory. Landé seems to have made progress in this direction, by postulating coupled orbits. Thus according to Landé, the eight electrons of an octet move in such a way that their positions are always symmetrically located with respect to each of three mutually perpendicular planes which pass through the nucleus. Landé offers no suggestions as to a cause or mechanism of this coupling.

The chemical evidence indicates that there is not only a definite coupling between the electrons in a single shell but also between electrons in different shells. Thus the octet exists only about nuclei which already have stable pairs. The magnetic properties of the elements furnish excellent proof of electron coupling between different shells. Such action is not taken into account in Landé's theory.

The most striking case of electron coupling seems to be that in the helium atom. Since the underlying mechanism must be essentially similar to that of the octet, it would seem that a study of the structure of the helium atom offers the most promising method for the attack on the problem of the mechanism of quantum phenomena.

Bohr's work on the structure of atoms and molecules has been based on the assumption that "the dynamical equilibrium of the systems in the stationary states is governed by the ordinary laws of mechanics" while the quantum laws apply to "the passing of the systems between different stationary states." For each degree of freedom there is an infinite number of solutions of the dynamical problem, but as Sommerfeld has shown, there are as many quantum conditions to be fulfilled as there are degrees of freedom. As a result, there is only a discrete number of possible solutions. These fundamental postulates have received such strong support from the work of Bohr, Sommerfeld and others that there seems to be no reason to doubt their general validity.

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[1] See particularly *Proc. Natl. Acad. Sci.* **5**, 252 (1919).

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According to the theory which I advanced in 1919 (Postulates 1, 3 and 4, *l.c.*) the electrons in their most stable positions move only within certain limited regions or "cells" within the atom. In the atoms of the inert gases the cells were found to be arranged symmetrically with respect to an equatorial plane, no electrons however lying in this plane. From this viewpoint the two electrons in the helium atom should not move in the same orbit but in separate orbits located symmetrically with respect to the equatorial plane. Let us consider the most probable motions of this kind.

Sommerfeld has shown[1] that in general a single electron in an atom must fulfill three quantum conditions corresponding to its three degrees of freedom. Choosing coördinates like those used on the earth we may describe the position of an electron in terms of its latitude, longitude and distance from the center of the atom. In ordinary helium, with the atoms in their most stable state, we must assume that each electron has only one quantum, and that this quantum corresponds to some one of the three degrees of freedom. Radial motion such as rectilinear motion along the polar axis, is to be excluded[2]

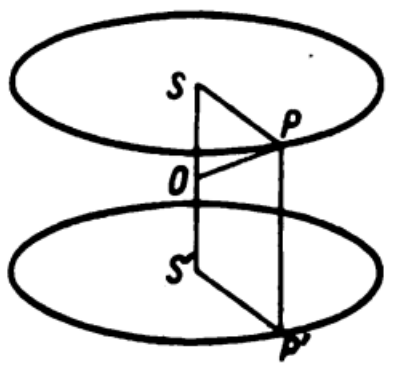

FIG. 1. Double-circle model for the helium atom.

since the electrons would have to pass through the nucleus. We have then to consider motion either in longitude or in latitude.

Motion in Longitude. Double Circle Model.—If the electrons move in longitude only, they will travel along parallels of latitude and rotate in the same direction in circular orbits in two parallel planes equidistant from the equatorial plane, as is shown in Fig. 1. Let r be the distance from the nucleus of the atom (at O) to one of the electrons P; let b be the distance OS or half the distance between the planes of the orbits; and let a be the radius SP of the orbits. Since in the helium atom the nucleus has the charge $2e$, the force of attraction between the nucleus and each electron is $2e^2/r^2$. The component of this force directed towards the other electron is $2e^2b/r^3$ while the repulsive force between the electrons is $e^2/4b^2$. Equating these, we find $r = 2b$ as a condition for dynamical equilibrium; the latitude of the electrons must therefore be 30°.

If ω is the angular velocity of the electron in its orbit, the centrifugal force exerted by it is $ma\omega^2$, where m is the mass of the electron. The com-

[1] *Atombau*, 1st edit., p. 411 (1919).

[2] *Atombau*, p. 273.

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ponent of the attractive force of the nucleus in the direction towards the center of the orbit (PS) is $2e^2a/r^3$. Equating these forces we obtain:

$$m\omega^2 r^3 = 2e^2. \tag{1}$$

This is as far as we can proceed by means of the classical mechanics. We still have two unknown quantities and therefore cannot determine the constants of the model.

If we impose the quantum condition that the angular momentum of the electron about the center of its orbit shall be $h/2\pi$ we find

$$2\pi m a^2 \omega = h. \tag{2}$$

These two equations, together with the relation $r = 2a/\sqrt{3}$ give:

$$a = \frac{h^2}{3\sqrt{3}\pi^2 me^2} = \frac{4}{3\sqrt{3}} a_0, \tag{3}$$

$$\omega = \frac{27\pi^3 me^4}{2h^3} = \frac{27}{16}\omega_0. \tag{4}$$

Here a_0 and ω_0 are the values of a and ω for the hydrogen atom as found by Bohr, namely:

$$a_0 = \frac{h^2}{4\pi^2 me^2}, \tag{5}$$

$$\omega_0 = \frac{8\pi^3 me^4}{h^3}. \tag{6}$$

Since Bohr has shown that the kinetic energy of the electrons is numerically equal to half the potential energy but opposite in sign, we may place the kinetic energy equal to W and thus find from (3) and (4).

$$W = \frac{27}{4}\frac{\pi^2 me^4}{h^2} = \frac{27}{8} W_0. \tag{7}$$

Here W_0 is the value of W corresponding to the hydrogen atom:

$$W_0 = \frac{2\pi^2 me^4}{h^2} = \frac{e^2}{2a_0}. \tag{8}$$

Taking $h = 6.554\times10^{-27}$ erg second; $e = 4.774\times10^{-10}$ e.s. units; and $m = 9.002\times10^{-28}$ grams, we find the following numerical values
$a_0 = 0.5304\times10^{-8}$ cm,
$\omega_0 = 4.134\times10^{16}$ radians per second (6.580×10^{15} revolutions per second).
$W_0 = 2.157\times10^{-11}$ erg which corresponds to 312,000 g calories per g molecule. W_0/e is equivalent to 13.55 volts.

Bohr has shown that for the positively charged helium ion $W = 4W_0$. Comparing this with equation (7) we see that the helium model that we have been considering is unstable as it would lose one of its electrons and form

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a positively charged helium ion. The ionizing potential would thus be negative in sign and its value would correspond to $3.375W_0 - 4W_0 = -0.625W_0$ or -8.5 volts.[1]

This model therefore cannot represent the atom of ordinary helium, although it may well correspond to a possible disturbed state of the atom. There is the same objection to this model as to the Bohr model in regard to the momentum of the atom as a whole about its axis of symmetry, for the work of Lenz seems to show that there should be no momentum in the most stable atoms.

Motion in Latitude. Oscillating, or Semi-circular Model.—Let us consider the case that the electrons have no component of motion in longitude. The motion is thus confined to the plane of a meridian of our system of coördinates. In Fig. 2 let FF' represent the polar axis and the circle $BEB'E'B$ a meridian circle. The intersection of the equatorial plane with the plane of the meridian is the line AOA'. If we imagine two electrons at P and P' symmetrically placed with respect to the line AA', we can conceive of a series

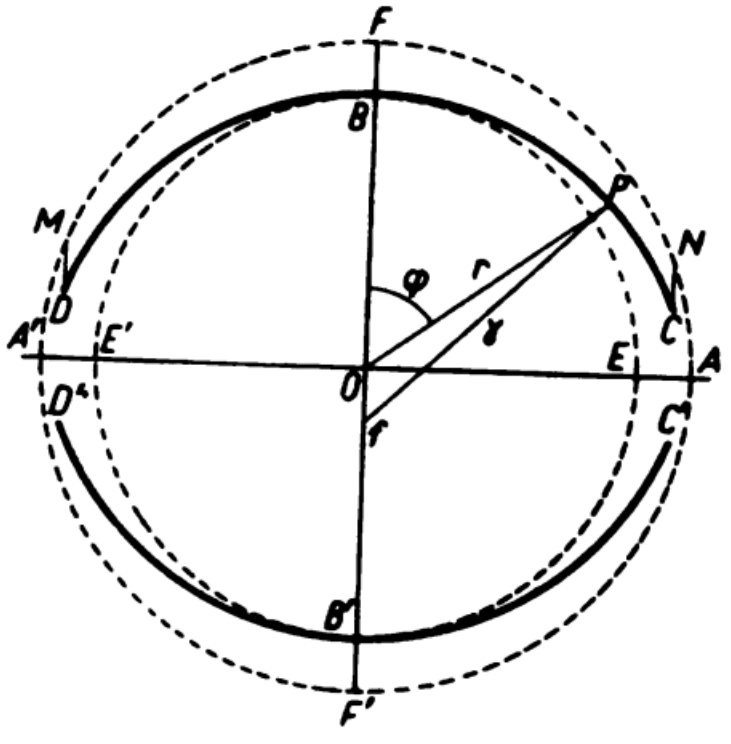

FIG. 2. Oscillating or semi-circular model for the helium atom.

of orbits consistent with the ordinary mechanics. We are concerned here with those in which there is as little radial motion as possible. We shall now proceed to show that a motion of the electrons back and forth along the lines CBD and $C'B'D'$ respectively is in accord with the laws of mechanics. This motion corresponds to that of the two electrons in the circular ring of Bohr's model for the helium atom except that the electrons revolve in opposite directions about the nucleus. If we were dealing with electrons having more than one quantum, we should have to consider paths which bear the same relation to elliptical orbits that the paths CBD and $C'B'D'$ bear to the circular orbits of Bohr's model.

[1] By a misprint this appeared as -5.8 volts in the preliminary notice in *Science*.

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The electron at P is attracted by the nucleus at O and repelled by the electron at P'. Let N be the atomic number of the nucleus at O; it thus has the positive charge Ne. In moving the two electrons from infinity to the positions P and P' the work done by the attraction of the nucleus is $2\,Ne^2/r$ while the work that must be done against the repulsion of the electrons is $e^2/(2r\cos\varphi)$, where r is the distance PO and φ is the angle BPO. Hence the potential energy E_p of *one electron* is

$$E_p = -\frac{e^2}{r}\left(N - \frac{1}{4\cos\varphi}\right) \tag{9}$$

and the kinetic energy E_k is

$$E_k = \frac{m}{2}\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\varphi}{dt}\right)^2\right]. \tag{10}$$

The equations of motion for the electrons are most easily obtained by Hamilton's method. If q is any coördinate, we place $q' = dq/dt$ and define p by[1]

$$p = \frac{\partial E_k}{\partial q'}. \tag{11}$$

Letting q be successively equal to r and to φ we find from (11) and (10)

$$p_r = m\frac{dr}{dt}, \qquad p_\Phi = mr^2\frac{d\varphi}{dt}. \tag{12}$$

The Hamilton function H is obtained by expressing $E_p + E_k$ in terms of q and p. Thus (9), (10) and (12) give

$$H = \frac{\mathrm{I}}{2m}\left(p_r^2 + \frac{p_\varphi^2}{r^2}\right) - \frac{e^2}{r}\left(N - \frac{1}{4\cos\varphi.}\right). \tag{13}$$

The equations of motion are then found by means of the relation[1]

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q} \tag{14}$$

from (12) and (13) as follows (after dividing by m and mr^2 respectively):

$$\frac{d^2r}{dt^2} = r\left(\frac{d\varphi}{dt}\right)^2 - \frac{e^2}{mr^2}\left(N - \frac{1}{4\cos\varphi}\right), \tag{15}$$

$$\frac{d^2\varphi}{dt^2} = -\frac{e^2}{4mr^3}\frac{\sin\varphi}{\cos^2\varphi} - \frac{2}{r}\frac{d\varphi}{dt}\frac{dr}{dt}. \tag{16}$$

Since it is impossible, by the classical mechanics alone, to find the absolute dimensions of this model, it will be convenient to express the above equations in terms of variables which depend only on relative dimensions.

[1] See Sommerfeld, *Atombau*, p. 216.

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It is evident from (16) and from considerations of symmetry that the electrons move with the maximum angular velocity when they are at the mid-points of their paths that is, when $\varphi = 0$. Let us then choose the unit of time so that this maximum angular velocity φ_0' shall be unity. If we let θ be the time expressed in these new units we have

$$\theta = \varphi_0' t. \tag{17}$$

Similarly let us take as our unit of length, r_0 the radius vector BO at the mid-point of the path. Let ϱ represent the radius vector at the point P expressed in the new units. Then

$$\varrho = \frac{r}{r_0}. \tag{18}$$

By making these substitutions in equations (15) and (16) we are able to reduce them to the form

$$\frac{d^2\varrho}{d\theta^2} = \varrho\left(\frac{d\varphi}{d\theta}\right)^2 - \frac{1}{a\varrho^2}\left(N - \frac{1}{4\cos\varphi}\right), \tag{19}$$

$$\frac{d^2\varphi}{d\theta^2} = -\frac{1}{4a\varrho^3}\frac{\sin\varphi}{\cos^2\varphi} - \frac{2}{\varrho}\frac{d\varrho}{d\theta}\frac{d\varphi}{d\theta}, \tag{20}$$

where

$$a = \frac{mr_0^3(\varphi_0)^2}{e^2}. \tag{21}$$

The total energy of the molecule is $2(E_p + E_k)$ and we may place this equal to $-W$ and thus obtain from (9), (10), (17), (18), and (21):

$$\frac{Wr_0}{e^2} = \frac{2}{\varrho}\left(N - \frac{1}{4\cos\varphi}\right) - a\left[\left(\frac{d\varrho}{d\theta}\right)^2 + \varrho^2\left(\frac{d\varphi}{d\theta}\right)^2\right]. \tag{22}$$

At the mid-point of the path (B in Fig. 2) we may place $\varphi = 0$, $\varrho = 1$, $d\varrho/d\theta = 0$, and $d\varphi/d\theta = 1$. Since the total energy W is constant we may substitute these values in (22) and obtain

$$\frac{Wr_0}{e^2} = 2N - \frac{1}{2} - a. \tag{23}$$

Combining this with (22) gives

$$a\left[\left(\frac{d\varrho}{d\theta}\right)^2 + \varrho^2\left(\frac{d\varphi}{d\theta}\right)^2\right] = \frac{2}{\varrho}\left(N - \frac{1}{4\cos\varphi}\right) + a - 2N + \frac{1}{2}. \tag{24}$$

This equation together with (19) defines the motion of the electrons in this model. It is necessary to resort to numerical calculations in order to obtain ϱ and θ as functions of φ. Table I gives the results of such calculations. The procedure was as follows:

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As a first approximation ϱ was assumed constant and equal to unity so that $d\varrho/d\theta$ and $d^2\varrho/d\theta^2$ were taken to be zero. Equations (19) and (24) then take simple forms. Placing $N = 2$ for helium, equation (19) gives for $\varphi = 0$, the result $\alpha = 7/4$. By using this value of α approximate values for $d\varphi/d\theta$ as a function of φ can then be calculated from equation (24). By substituting these in (19) approximate values for $d^2\varrho/d\theta^2$ can be found. By dividing these by $d\varphi/d\theta$ and by approximate integration with respect to φ we obtain the radial velocity $d\varrho/d\theta$ as a function of φ. The end of the path (C in Fig. 2) is determined by finding the point at which $d\varphi/d\theta$ is zero. If the electrons are to return back along the same path it is evidently necessary that $d\varrho/d\theta$ and $d\varphi/d\theta$ shall vanish for the same value of φ. Because of the approximate nature of the calculations this condition will not be met and it is therefore necessary to adjust the values of $d\varrho/d\theta$ so that they become zero at the point C. By dividing these adjusted values by $d\varphi/d\theta$, and by approximate integration with respect to φ, we obtain ϱ as a function of φ. The values of θ as a function of φ are obtained by integrating the reciprocal of $d\varphi/d\theta$ with respect to φ. From the adjusted values of $d\varrho/d\theta$ the second derivative $d^2\varrho/d\theta^2$ at the point $\varphi = 0$ is calculated. Substituting this in (19) gives a second approximation for α. Using this and the values of ϱ and $d\varrho/d\theta$ already obtained, we then proceed by (24) and (19) to obtain second approximations of $d\varphi/d\theta$ and $d^2\varrho/d\theta^2$ in a similar manner. This process may be repeated until sufficient accuracy has been obtained.

The numerical calculations were carried out with the aid of a calculating machine to five or six figures. The integrations were done by Simpson's rule or more often by Weddle's rule and special methods were adopted to increase the accuracy in the region close to the end of the path. Four series of approximations were carried out and it is believed that the results which are recorded in Table I are accurate to about one tenth per cent.

By plotting ϱ and φ as polar coördinates as in Fig. 2, it is seen that the path DBC of the electron is very nearly an arc of circle whose center lies at some point F on the line OB'. If we let γ be the distance from F to the moving point P and if ε is the distance OF then we have

$$\gamma = \varrho^2+\varepsilon^2+2\varrho\varepsilon\cos\varphi. \tag{25}$$

Let us choose the point F so that γ is the radius of curvature of the path DBC at the point B. Then the first and second derivatives of γ with respect to θ will be zero when φ is zero, and for this point we may also place $\varrho = 1$;

$$\frac{d\varrho}{d\theta} = 0 \qquad \text{and} \qquad \frac{d\varphi}{d\theta} = 1.$$

We thus obtain

$$\left[\frac{d^2\varrho}{d\theta^2}\right]_{\varphi=0} = \frac{\varepsilon}{1+\varepsilon}. \tag{26}$$

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TABLE I

Data for the Motion of the Electrons in the Second Model of the Helium Atom
$\alpha = 2.0920$

φ Radians	θ	$\frac{d\varphi}{d\theta}$	ϱ	$\frac{d\varrho}{d\theta}$
0.00	0.0000	1.0000	1.0000	0.0000
0.10	0.1001	0.9979	1.0008	0.0165
0.20	0.2006	0.9912	1.0033	0.0325
0.30	0.3020	0.9802	1.0074	0.0480
0.40	0.4048	0.9646	1.0131	0.0628
0.50	0.5095	0.9448	1.0204	0.0765
0.60	0.6168	0.9201	1.0292	0.0887
0.70	0.7271	0.8913	1.0396	0.0992
0.80	0.8417	0.8558	1.0515	0.1074
0.90	0.9612	0.8162	1.0647	0.1131
1.00	1.0881	0.7633	1.0792	0.1146
1.10	1.2245	0.6974	1.0947	0.1114
1.20	1.3784	0.6019	1.1110	0.0995
1.25	1.4659	0.5305	1.1193	0.0885
1.30	1.5712	0.4425	1.1276	0.0701
1.31	1.5957	0.3925	1.1293	0.0650
1.32	1.6224	0.3578	1.1310	0.0591
1.33	1.6520	0.3164	1.1326	0.0521
1.34	1.6864	0.2648	1.1342	0.0434
1.35	1.7300	0.1944	1.1359	0.0318
1.355	1.7596	0.1434	1.1367	0.0234
1.36	1.8110	0.0513	1.1375	0.0085
1.3607	1.8394	0.0000	1.1376	0.0000

By comparing this with equation (19) we find since $N = 2$

$$\gamma_0 = 1+\varepsilon = \frac{4}{7}\alpha, \tag{27}$$

where γ_0 is the value of γ corresponding to $\varphi = 0$ (BF in Fig. 2). Placing $\alpha = 2.0920$ this gives $\varepsilon = 0.1954$ and $\gamma_0 = 1.1954$. Taking this value of ε we can now calculate γ for other values of φ by equation (25). Table II shows that γ, the radius vector from the point F, is almost exactly constant or in other words the path DBC is nearly an arc of a circle with F as its center.

TABLE II

Radius Vector from the Point F

φ	0.00	0.50	1.00	1.20	1.25	1.36073
γ	1.1954	1.1954	1.1959	1.1956	1.1953	1.1937

To determine the absolute dimensions of this model we must now apply the quantum theory. The completely successful applications of the quantum theory to atomic structure have been limited to atoms having only one elec-

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tron. There is therefore no certainty as to how this theory should be formulated for the case of the more complicated atoms. Bohr assumes[1] that "the 'permanent' state of any atomic system is determined by the condition that the angular momentum of every electron round the center of its orbit is equal to $h/2\pi$," but this is supposed to apply only to circular orbits. In the present case the momentum of each electron varies from zero to a maximum so that it might seem at first sight that Bohr's assumption is not applicable. However it is an attractive hypothesis to assume that in the case of coupled electrons, the quantum theory is concerned not with the angular momentum possessed by one electron but rather with the angular momentum which, by being transferred from electron to electron, circulates in each of two directions about the nucleus. The discrete nature of quanta suggests that units of angular momentum have something analogous to independent physical existence. In the model we are considering we may imagine that when the electrons are at the midpoints of their paths, each possesses one quantum of angular momentum. As the electrons move, the velocity decreases, but we may consider that the momentum, instead of disappearing, is transferred from one electron to the other. Thus when the electrons have reached the ends of their paths, the momentum is not zero but each electron has one half quantum of clockwise and one half quantum of counter-clockwise angular momentum. One advantage of this viewpoint is that it indicates a very close analogy between Bohr's model and the model under consideration.

Let us therefore place the angular momentum of the electrons at the midpoint of their orbits equal to $h/2\pi$:

$$2\pi m r_0^2 \varphi_0' = h. \tag{28}$$

Whence by (21) and (5) we find

$$r_0 = \frac{a_0}{\alpha}. \tag{29}$$

The energy of the atom is then found by substituting this and $N = 2$ in (23) and combining with (8):

$$W = W_0 \alpha(7 - 2\alpha). \tag{30}$$

From (28), (29), (5) and (6) we obtain

$$\varphi_0' = \alpha^2 \omega_0. \tag{31}$$

Placing $\alpha = 2.0920$ gives us the absolute dimensions of the helium atom according to this model:

$$\begin{aligned} r_0 &= 0.4780 a_0 &&= 0.2535 \times 10^{-8} \text{ cm}, \\ W &= 5.8911 W_0 &&= 1.2707 \times 10^{-10} \text{ erg}, \\ \varphi_0' &= 4.3765 \omega_0 &&= 1.8094 \times 10^{17} \text{ radians per sec.} \end{aligned} \tag{32}$$

[1] *Phil. Mag.* **26**, 875 (1913).

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From these results we can now calculate from Table I the data for the motion of the electrons in absolute units. Thus to express time coördinate in seconds we divide θ by the above value of φ_0'. The angular velocity at any point is found by multiplying $d\varphi/d\theta$ by φ_0'. The radius vector is expressed in cm by multiplying ϱ by r_0 and the radial velocity is obtained by multiplying $d\varrho/d\theta$ by $r_0\varphi_0'$ which is the linear velocity of the electrons as they pass the midpoint of their paths (4.587×10^8 cm per sec). The time taken for one complete oscillation of the electrons is thus 4.067×10^{-17} seconds, while the number of oscillations per second is 2.459×10^{16}.

The energy of the singly charged helium ion according to Bohr is $W = 4W_0$. The difference between this and the value of W which we have found for our model ($1.8911\times W_0$) corresponds to the energy required to ionize the helium atom. Expressing this in volts we obtain for the ionizing potential of helium the value 25.62 volts. This agrees with Frank and Knipping's value 25.4 ± 0.25 volts within the probable experimental error. Horton and Davies[1] found the ionizing potential to be 25.7 volts, and K. T. Compton, in a very recent paper,[2] finds 25.5 volts.

In Bohr's model for the helium atom the distance between the electrons remains constant. For this case, we may place in (19) $\cos\varphi = 1$; $\varrho = 1$, and $d\varphi/d\theta = 1$, and thus obtain

$$\alpha = N - \tfrac{1}{4}.$$

For the helium atom placing $N = 2$ we find $\alpha = 7/4$. By substituting this value of α in equations (29), (30) and (31) we obtain that same values[3] for r, W and ω that Bohr found for the helium atom,[4] namely:

$$\begin{aligned} r_B &= \tfrac{4}{7}a_0 &&= 0.3031\times10^{-8}\text{ cm},\\ W_B &= \tfrac{4}{8}\tfrac{9}{}W_0 &&= 1.321\times10^{-10}\text{ erg},\\ \omega_B &= \tfrac{4}{16}\tfrac{9}{}\omega_0 &&= 1.266\times10^{17}\text{ radians per sec},\\ & && (2.015\times10^{16}\text{ revolutions per sec}). \end{aligned} \tag{33}$$

According to Bohr's model, the energy needed for ionization is $W_B - 4W_0$ and the ionization potential is thus 28.79 volts. This is 3.4 volts higher than Frank and Knipping's value and is thus not to be reconciled with their experiments.

We have seen from Table II that the path of an electron in the oscillating model is nearly an arc of a circle whose radius γ_0 is given by equation (27). Multiplying this by the value of r_0 as given by equation (29) we obtain $(4/7)a_0$ as the absolute value of this radius. By comparison with (33) we see

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[1] *Proc. Roy. Soc.* A **95**, 408 (1919).

[2] *Phil. Mag.* **40**, 553 (1920).

[3] In a similar manner we may obtain Bohr's data for the hydrogen atom from (29), (23) and (31) by placing $\alpha = 1$ and $N = 1$.

[4] *Phil. Mag.* **26**, 489 (1913).

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that this is identical with r_B the radius of the orbit of the electrons in Bohr's model. We thus obtain the extraordinary result that notwithstanding the complicated nature of the interaction between the two electrons in the oscillating model, the paths of the electrons consist of unaltered portions of the circular orbits of the Bohr model which are merely displaced bodily along the diameter of the Bohr orbit as indicated in Fig. 2. The circle $AFA'F'$ represents the orbit of the Bohr model. The path CBD of the oscillating model (drawn to scale) is obtained by taking a portion NFM of the Bohr orbit and displacing it by the distance FB in the direction of the radius FO. The distances MD and NC are thus equal to FB, which is 0.1635 of the distance FO. The angle φ corresponding to the end of the path (at C) is 1.3607 radians or 77° 57′ 45″.

The above close relationship between the oscillating model and the Bohr model seems to constitute additional justification for the quantum assumption we have made. It is of interest to enquire, however, what results are obtained if the quantum condition is formulated in other ways?

Sommerfeld and others express the quantum condition by the equation

$$\int p\, dq = nh, \tag{34}$$

where q is a generalized coördinate and p is defined by equation (11). For the kind of model we are considering I have not been able to find any general method for determining what coördinates should be used. Let us try, however, to calculate the ionizing potential of helium by two different quantum assumptions, viz.:

1. Let $q = \varphi$, so that we apply (34) to the angular momentum of the electrons about the nucleus. Then p is given by (12) and we then find by (17), (18) and (34), placing $n = 1$:

$$2\pi m r_0^2 \varphi_0' P = h, \tag{35}$$

where P is equal to P_1 defined by the equation

$$2\pi P_1 = \int \left(\frac{d\varphi}{d\theta}\right) \varrho^2 d\varphi. \tag{36}$$

The integration is to be carried over a complete cycle. Equation (36) reduces to (28) if $P = 1$.

2. Let q represent the distance between P and B along the path DBC (Fig. 2). The quantum condition then becomes

$$\int m v\, ds = h, \tag{37}$$

where v is the linear velocity of the electron at the point P and s is the distance along the path that separates the point P from the midpoint B. This can be reduced to (35) if we place P equal to P_2 which is defined by

$$2\pi P_2 = \int \left[\left(\frac{d\varrho}{d\theta}\right)^2 + \varrho^2 \left(\frac{d\varphi}{d\theta}\right)^2\right] d\theta. \tag{38}$$

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From equation (35), by methods similar to those used in the derivation (29) and (30), we obtain

$$r_0 = \frac{a}{\alpha P^2}, \tag{39}$$

$$W = \alpha(7-2\alpha)P^2 W_0. \tag{40}$$

The values of P can be found by approximate integration from the data of Table I but P_2 can also be calculated in terms of α as follows. By comparison of (38) with (10) and (22) we find that the quantity in brackets is equal to $2E_k r_0/\alpha e^2$. By reference to (17) and (23), placing $N = 2$ we then obtain

$$2\pi P_2 = \frac{(7-2\alpha)\varphi_0'}{\alpha W}\int \mathrm{E}_K dt\,.$$

But

$$\int E_k dt = 4\bar{E}_k t_c\,,$$

where $\bar{E}_k$ is the time average of the kinetic energy of each of the electrons, and t_c is the time taken by an electron to move from B to C. Bohr and Sommerfeld have shown that the total energy $(-W)$ of any atom is equal to the mean kinetic energy with its sign reversed. Therefore $2\bar{E}_k = W$ and by considering (17) we then find

$$P_2 = \frac{(7-2\alpha)\theta_c}{\pi\alpha}. \tag{41}$$

Placing $\alpha = 2.0920$ and $\theta_c = 1.8394$ (Table I), we thus obtain $P_2 = 0.7881$. By approximate integration of equation (38) by the data of Table I we find $P_2 = 0.7886$. The closeness of this agreement affords a check on the accuracy of the data in Table I. Substituting the value of P_2 in (40) we find W and thus calculate the ionizing potential as -4.58 volts.

In a similar way we find from (36) $P_1 = 0.7807$ which gives an ionizing potential of -5.55 volts.

The oscillating model for the helium atom is thus not compatible with the formulation of the quantum theory given by equation (34). On the other hand the success in calculating the ionizing potential by assuming the angular momentum at the midpoint of the path to be $h/2\pi$, as well as the remarkable relationships with the Bohr model which were developed, lend strong support to the oscillating type of model and suggest new directions in which the quantum theory may be applied to atoms and molecules containing more than one electron.

The real test for the new model will probably be obtained through a study of the spectrum of helium in the neighborhood of 590 Å for this spectrum should make it possible to calculate the ionizing potential with very high accuracy. It is also desirable to test the model by calculating other atomic properties such as refractive index, absorption and ionization by X-rays. The mathematical difficulties appear rather serious but by no means insuperable. It is hoped that the data of Table I may prove to be of service in such calculations.

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THE STRUCTURE OF THE STATIC ATOM

Science
Vol. LIII, No. 1369, 290, March (1921).

IN ATTEMPTING recently to derive the conditions which determine the stability of chemical molecules I was impressed by the importance of the part played by Coulomb's law of inverse square forces between charged particles. In fact, by considering a static arrangement of electrons according to the models which I proposed two years ago, and calculating the total potential energy by Coulomb's law, I have found it possible not only to determine the relative stability of various substances but to calculate with reasonable accuracy the heats of formation of compounds even of widely varying types.

In all such calculations, however, it is necessary to assume that the electrons are kept from falling into the nucleus by some undetermined force, for Coulomb's law alone can not account for this. According to Bohr's theory of atomic structure, the requisite repulsive force is nothing more than centrifugal force due to rotation of the electrons about the nucleus. This theory has been so remarkably successful in accounting for the spectra of hydrogen and helium that the fundamental assumption of movement about the nucleus has seemed justified, notwithstanding the fact that this violates all our classical laws regarding the radiation of energy from accelerated electrons.

From the chemical point of view it is a matter of comparative indifference what the cause of the repulsive force is, so long as it exists. I therefore endeavored to find what law of repulsive force between electrons and positive nuclei would produce an effect equivalent to the centrifugal force of Bohr's theory.

According to Bohr the average kinetic energy in any atom or molecule is half as great as the average potential energy, but opposite in sign. I therefore now assume that this energy, which Bohr called kinetic, is another form of potential energy dependent upon certain quantum changes in the electron. From this potential energy it is then easy to determine the law of repulsive force.

The result of this analysis is that we may regard the force between any nucleus of charge Ze and an electron of charge e as consisting of two parts which act independently. The first is the Coulomb attractive force F_e given by

$$F_e = \frac{Ze^2}{r}. \qquad (1)$$

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The second force, which we may call the *quantum force* is a repulsive force F_q given by

$$F_q = \frac{1}{mr^3}\left(\frac{nh}{2\pi}\right)^2. \tag{2}$$

In these equations r is the distance between the electron and the nucleus, m is the mass of the electron, h is Planck's quantum, and n is an integer denoting the quantum state of the electron. This repulsive force, varying inversely as the cube of the distance, is remarkable in that it is independent of the charge on the nucleus. It is to be noted especially that an electron which has not undergone any quantum change and for which therefore $n = 0$, follows Coulomb's law accurately. Thus presumably β-rays in passing through an atom will be acted on only by the usual law.

It can be readily shown that under the influence of these two forces an electron will be in stable equilibrium when it is at a distance from the nucleus equal to

$$a = \frac{n^2 a_0}{Z}, \tag{3}$$

where a_0 is given by

$$a_0 = \frac{h^2}{4\pi^2 m e^2}. \tag{4}$$

This result is identical with that for the radius of the orbit in Bohr's theory, but of course the law of force was chosen to give just this result.

If W is the total energy of the system with its sign reversed we obtain

$$\frac{W}{W_0} = \frac{2Za_0}{r} - \frac{n^2 a_0^2}{r^2}, \tag{5}$$

where

$$W_0 = \frac{2\pi^2 m e^4}{h^2}. \tag{6}$$

Equation (5) has no equivalent in Bohr's theory for it applies to the transitions between stationary states. The first term in the second member represents the Coulomb potential while the second corresponds to the quantum potential.

When an electron has settled down into its position of equilibrium, the value of W becomes

$$W = \frac{Z^2 W_0}{n^2}. \tag{7}$$

This also is identical with the result obtained by Bohr for the total energy in any stationary state. It follows from this that the Rydberg constant, the Balmer series and all other series calculated by Bohr can be obtained by this method without assuming electrons moving about the nucleus.

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If the electron is disturbed from its position of equilibrium it oscillates about this position. From equation (5) the frequency of this oscillation is found to be

$$v = \frac{4\pi^2 Z^2 m e^2}{n^3 h^3}. \tag{8}$$

This is identical with the frequency of revolution of the electron in Bohr atom. From this we may draw a definite physical picture of the mechanism of the transition between two states, at least when Z is large. Bohr has shown that under these conditions the frequency radiated when an electron passes from one circular orbit to the next inner one is the same as the frequency of revolution. According to the present theory, if the quantum number of an electron in a stable position decreases by one unit, the electron is no longer stable but falls towards its new position of equilibrium, and oscillates about this position. It then radiates its energy of oscillation according to the usual laws of electro-dynamics.

One of the greatest successes of the Bohr theory is that it accounts for certain slight differences between hydrogen and helium lines by the nuclear mass correction. This correction is taken care of in the present theory with the same accuracy if we assume a slight modification to our law of quantum repulsion, viz. replace equation (2) by

$$F_e = \left(\frac{nh}{2\pi}\right)^2 \frac{\frac{1}{m} + \frac{1}{M}}{r^3}, \tag{9}$$

where M is the mass of the nucleus. This seems to indicate that the quantum force is due to an interaction between the electron and the nucleus in which both masses play a similar role. For example, it may be imagined that both are set into rotation in opposite directions about the axis connecting them.

Sommerfeld has accounted for the fine-line structure of spectral lines by considering a relativity correction due to the rapid motion of the electron. This would seem to be excellent proof that the electrons do move. However, it is possible that the motion resides within the electron and nucleus. It is probably significant that the relativity correction can be taken into account in the present theory if we substitute in equation (2) in place of n^2 the expression

$$(n_e + n_r)^2 - \alpha^2 Z^2 \left(\frac{n_r}{n_e} + \frac{1}{4}\right). \tag{10}$$

where α is a constant calculated by Sommerfeld. A consideration of this equation may lead to more definite conceptions of the structure of the electron and nucleus. The quantities n_e and n_r refer to what Sommerfeld calls angular and radial quanta. It is not yet clear just what interpretation is to be placed upon these in the present theory but they are evidently only of secondary importance in determining the forces between the electrons and the nucleus.

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When we consider other atoms such as helium it seems as if the new theory may lead us much further then the usual theory, for the determination of equilibrium positions under static forces is extremely simple compared to the corresponding dynamical problem. Furthermore we are not troubled by mysterious quantum conditions which are theoretically applicable only to periodic orbits while the calculated orbits in atoms are not periodic.

At present I am studying the spectra of helium and lithium from this viewpoint. The following tentative conclusions may be stated.

The quantum force between quantized electrons is not as simple as between electrons and nuclei. The quantum force between electrons on opposite sides of a nucleus is one of repulsion whose magnitude is approximately given by equation (2) if the quanta are all of the "angular" type, but is considerably less when the quanta are of the "radial" type. But if the electrons are on the same side of the nucleus, the quantum force between electrons is one of attraction, also given approximately by equation (2). Thus if one of the electrons in the helium is uniquantic, and the other one is diquantic, the latter can take equilibrium positions either on the opposite side of the nucleus from the uniquantic electron or on the same side. This perhaps explains the fact that helium (as well as other elements with two outer electrons such as calcium, etc.) has two separate complete sets of spectra (helium and parhelium). It is also in accord with the remarkable facts in regard to the helium spectrum which were recently pointed out by Franck and Reiche.

These properties of the electron are in full accord with those which are needed to account for chemical relationships. The new theory fulfills the predictions of G. N. Lewis who in 1916 wrote[1] in reference to Bohr's theory:

"Now this is not only inconsistent with the accepted laws of electromagnetics but, I may add, is logically objectionable, for that state of motion which produces no physical effect whatsoever may better be called a state of rest."

It is also in accord with the conclusion which I gave in a paper entitled "The properties of the electron as derived from the chemical properties of the elements",[2] viz.:

"How can these results be reconciled with Bohr's theory and with our usual conception of the electron? It is too early to answer. Bohr's stationary states and the cellular structure postulated above have many points of similarity. It seems that the electron must be regarded as a complex structure which undergoes a series of discontinuous changes while it is being bound by the nucelus or kernel of an atom. There seems to be strong evidence that an electron can exert magnetic attractions on other electrons in the atom even when not revolving about the nucleus of the atom."

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[1] *J. Am. Chem. Soc.* **38**, 773 (1916).

[2] *Phys. Rev.* **8**, 300 (1919).

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TYPES OF VALENCE

Science

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FROM the theory proposed by G. N. Lewis in 1916 and subsequently extended by the writer, it is clear[1] that the term valence has been used in the past to cover what we may now recognize as three distinct types of valence, viz.:

1. Positive valence: the number of electrons an atom can give up.
2. Negative valence: the number of electrons an atom can take up.
3. Covalence: the number of pairs of electrons an atom can share with its neighbors.

It was shown that these fundamental conceptions of valence as well as the actual numerical values of each type of valence for most of the elements could be derived from a few postulates regarding the structure of atoms. The following method of deriving these relationships, however, is not only much simpler than that previously given by the writer, but throws a new light on the relationships between the different types of valence.

We will take for granted the Rutherford type of atom, which consists of a positive nucleus surrounded by a number of electrons equal to the atomic number of the atom. We will also assume that Coulomb's law applies to the forces between the charged particles in the atom, but at the same time will recognize the existence of repulsive forces in atoms which prevent the electrons from falling into the nucleus. For the present purpose, however, it is immaterial whether the repulsive force is a dynamic force (centrifugal force) such as that assumed by Bohr, or is a static force as postulated by G. N. Lewis, J. J. Thomson or recently by the writer.[2]

We shall need to make only 3 postulates in regard to the structure of atoms, and these are consistent with those previously proposed.

Postulate 1.—*The electrons in atoms tend to surround the nucleus in successive layers containing* 2, 8, 8, 18, 18 *and* 32 *electrons respectively.*

The word atom is used in the broader sense which includes charged atoms (ions). If the number of electrons in an atom is such that they can not all form

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[EDITOR'S NOTE: This paper appears as Chapter Eighteen in the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

[1] Langmuir, *J. Am. Chem. Soc.* **41**, 926 (1919), and *J. Ind. Eng. Chem.* **12**, 386 (1920).

[2] *Science* **53**, 290, Mar. 25, 1921.

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nto *complete layers* in accord with Postulate 1, the extra electrons remain in the outside layer as an *incomplete layer* which we may designate as the *sheath* of the atom. Every electrically neutral atom must contain a number of electrons equal to the atomic number of the nucleus. If the outside layer of such an atom is nearly complete, the tendency expressed by Postulate 1 may cause a few additional electrons to be taken up in order to complete the layer, thus forming a negatively charged atom or ion. In such a case we may say that the sheath has been completed.

In the following discussion it is important to keep in mind this distinction between sheath and outside layer. Every incomplete outside layer which occurs normally is a sheath, but a complete outside layer may or may not be a sheath. The following definition will make this clearer. *The sheath of any atom* (*or atomic ion*) *consists of all the electrons in the outside layer provided that this layer is incomplete when the atom is electrically neutral.* Thus atoms of the inert gases (neon, argon, etc.) and ions such as Na^+, Ca^{++}, etc., have *no sheaths* for the outside layers of these atoms consist of electrons which already form a complete layer in the neutral atom. The sodium *atom*, however, has an *incomplete sheath containing* one electron, while the fluorine atom has an incomplete sheath of 7 electrons. The fluorine *ion*, on the other hand, has a *complete sheath* of 8 electrons.

The inert gases are the only elements whose neutral atoms have no sheaths, or in other words have all their electrons arranged in complete layers in accordance with Postulate 1. In all other atoms, the tendency expressed by this postulate can only be satisfied by an interaction between atoms involving a rearrangement of the electrons. This is to be regarded as the fundamental cause of chemical action and it is by such interaction that chemical compounds are formed.

When as the result of such rearrangement of electrons, the sheath of an atom has become complete, we may speak of the atom as a *complete atom*. Similarly if the interaction between atoms leads to complete satisfaction of the tendency of Postulate 1, so that all the atoms become complete, we may say that a *complete compound* is formed. We shall see that there are some factors which may oppose the formation of complete atoms and counteract the tendency of Postulate 1. In such cases incomplete atoms and compounds may result.

According to Postulate 1, the first complete layer in any atom consists of two electrons close to the nucleus. Let us call this stable pair of electrons a *duplet* and let us broaden the definition of duplet to include any pair of electrons which is rendered stable by its proximity to one or more positive charges. We may now state the second postulate.

Postulate 2.—Two atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms.

Let us now analyze the conditions that must be fulfilled if the interaction between atoms is to result in the formation of a complete compound.

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A given group of neutral atoms may interact to complete their sheaths in two ways:

1. *By transfer of electrons.*

a. Atoms having sheaths containing only a few electrons may give up these extra electrons to other atoms.

b. Atoms having nearly complete sheaths may take up electrons from other atoms.

2. *By sharing duplets.*

Atoms may share duplets with other atoms (Postulate 2) and thus complete their sheaths with fewer electrons than would otherwise be necessary.

Let e be the number of electrons in the sheath of any neutral atom and let s be the number of electrons in the sheath after the atom has interacted with others. For the atoms of any complete compound the values of s can be only 0, 2, 8, 18 or 32.

In any group of atoms, the only electrons available for the formation of the complete sheaths are those which orginally form the incomplete sheaths. The number of such electrons, $\Sigma(e)$, is found by adding the values of e for the individual atoms. In the resulting compound, if no duplets are shared by the atoms, the total number of electrons in the complete sheaths is $\Sigma(s)$. Every duplet held in common by two atoms, however, decreases by two the number of electrons required to form the sheaths. If then we let B be the total number of duplets shared within the given group of atoms, the number of electrons in the completed sheaths of the atoms of the compound is $\Sigma(s) - 2B$. Since this must equal the number in the original neutral atoms, we have the relation[1]

$$\Sigma(e) = \Sigma(s) - 2B. \tag{1}$$

This is the condition for the formation of a complete compound. We shall now proceed to put this equation into a simpler form and one which has more significance to the chemist.

The transfer of electrons that may occur during the interaction between atoms corresponds to what has been called positive and negative valence while the sharing of duplets corresponds to covalence. We shall see that the positive and negative valence differ from one another fundamentally only in algebraic sign, so that we shall find it convenient to include both positive and negative valence under the term *electrovalence*, which we may designate by the symbol v_e. We shall then adopt the convention that the electrovalence of an atom is positive when the atom gives up electrons and negative when it takes up electrons. The *electrovalence* of an atom in any compound may thus be defined as the number of electrons which the neutral atom must give up in forming that compound.

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[1] Equation (1) is a more general statement of the relation $e = 8n - 2p$ which has been used previously by the writer in discussing the "octet theory".

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If the neutral atom must *take up* electrons, the electrovalence is expressed as a negative number. The electrovalence of any atom is thus given by the expression

$$v_e = e - s. \tag{2}$$

Electropositive atoms in complete compounds lose all the electrons in their sheaths so that s is zero and therefore v_e is positive and equal to e. For electronegative atoms s is always greater than e so that v_e is negative.

Let us define the *covalence* (v_c) of an atom as the number of duplets which that atom shares with neighboring atoms. Every duplet shared by two atoms corresponds to a (covalence) *bond* between atoms, and we have already represented the number of such bonds in a given group of atoms by the symbol B. If we form $\Sigma(v_c)$ by adding the values of v_c for all the atoms in the given group, we count each bond twice. Hence we may place

$$\Sigma v_c = 2B. \tag{3}$$

By substituting (3) and (2) in (1) and rearranging terms we find

$$\Sigma v_e + \Sigma v_c = 0. \tag{4}$$

This simple result may be stated as follows:

The sum of the electrovalences and covalences for all the atoms in any complete compound is zero.

Electrovalence and covalence are thus in a sense supplementary to one another. If we represent $v_e + v_c$ by v, Equation 4 takes the form

$$\Sigma v = 0 \tag{5}$$

for any complete compound, and this suggests that the quantity v may have some simple physical significance.

In accordance with the nomenclature introduced by Lewis we may define the *kernel* of an atom as that part of an atom which remains after the sheath is removed. Since the neon atom has no sheath the whole atom constitutes a kernel with zero charge. The kernel of the sodium atom is the sodium ion with single positive charge, while the kernel of the fluorine atom (or fluorine ion) consists of the nucleus and two electrons, the whole having 7 positive charges.

Since the sheath of any neutral atom consists of e electrons, the positive charge on the kernel is also e. In any complete atom there are s electrons in the sheath. When the atom does not share duplets with other atoms (covalence zero) then the total charge of the atom is $e - s$. If, however, any two atoms hold a duplet in common the total charge of the two atoms is decreased by two units. *If the two atoms are substantially alike in size and structure*, we may assume that this decrease in charge is to be divided equally between the two atoms. Thus if an atom in a compound has s electrons in its sheath and it has a covalence v_c then the effective charge of its sheath is $s - v_c$. The total charge of the atom may thus be taken as

$$e - (s - v_c) = v_e + v_c = v.$$

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Thus v, the sum of the electrovalence and the covalence, for any atom in a compound, is equal to the *residual atomic charge*.

When two atoms which hold a duplet in common differ considerably in size, it is no longer obvious that the two electrons of the duplet should be divided equally between the two atoms in determining the residual charge. We may, however, arbitrarily so define the boundaries of the individual atoms in molecules that a duplet binding two atoms together is to be regarded as belonging equally to the two atoms. In this case we may consider v to be the residual atomic charge even when the atoms differ greatly in size.

It is evident from Coulomb's law that the separation of positive from negative charges requires in general the expenditure of work. The most stable forms of matter should be those in which the positive and negative charges are as near together as possible. However, we can not rely entirely upon Coulomb's law for this would indicate that the distance between unlike particles should decrease without limit. The exact distribution of charged particles in their most stable arrangement thus requires a knowledge of the repulsive forces whose existence we have already assumed. A further discussion of this point will be reserved for a future paper. At present we may attempt to express this relation by the following postulate.

Postulate 3.—*The residual charge on each atom and on each group of atoms tends to a minimum.*

By "residual charge" is meant the total charge of an atom or group of atoms regardless of sign. By "group of atoms" is meant any aggregate of atoms which are characterized by proximity to one another. It is felt by the writer that this postulate is a crude expression of a very important and fundamental law. When we understand the repulsive forces between charged particles better we shall be able to state the law in a more nearly quantitative form. The law is of very wide application. The uniformity of distribution of positive and negative ions in a salt solution is a familiar example of the working of this law. In any small finite element of volume the charges of the positive and negative ions tend to be very nearly equal or the residual charge tends to a minimum.

Postulate 3 expresses merely a strong *tendency* so that in general the charges of individual atoms are not necessarily zero. When the atomic charges depart from zero, however, they do so only as the result of a definite force or action which opposes the tendency of Postulate 3. We shall see that Postulates 1 and 3 are often in conflict and in such cases the tendency of Postulate 1 may prevail against that of Postulate 3.

We may now classify chemical compounds according to the types of valence exhibited by their atoms and will consider the application of Postulate 3 to each class of compound. There are 3 general subdivisions to consider:

(1) Complete Compounds, (2) Incomplete Compounds, and (3) Exceptional Cases.

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1. *Complete Compounds*

All electrons are in complete layers of 2, 8, 18 and 32 electrons, in accordance with Postulate 1. Since Σv_c in Equation (4) can never be negative, Σv_e must always be either zero or negative. Therefore atoms having negative valences must always be present in a complete compound. Thus electropositive elements do not form complete compounds with each other.

a. Compounds Without Covalence. — $\Sigma v_c = 0$. Equation (4) becomes $\Sigma v_e = 0$, so that the sum of the negative valences in the compound must be the same as the sum of the positive valences. Since the residual charge v for each atom must equal $v_e + v_c$ it is evident that compounds without covalence must consist of positively and negatively charged ions. The charge v on each ion of complete compounds of this type is uniquely determined by the values of e for the elements forming the ion. This is a case where Postulates 1 and 3 are in conflict. The tendency of Postulate 3 by itself would make each atom electrically neutral, but this would leave the sheaths of the atoms incomplete and so fail to satisfy the tendency of Postulate 1. The result is a kind of compromise by which Postulate 1 may be satisfied by the formation of complete compounds *provided this can take place without the charges on the ions becoming too large.*

Although Postulate 3 does not definitely fix the charges of the individual atoms in the compounds we are considering, yet it does determine the distribution of these ions in space. This is a factor of prime importance in the crystal structure, in the electrolytic conductivity of substances when in the liquid state, and in other properties. It is also the cause of an interesting effect observed when the number of ions of one sign is much greater than that of the other sign, as for example in such compounds as $AlCl_3$, PCl_5, SF_6, etc. Postulate 3 requires that the negative halogen atoms in these compounds shall surround the most strongly positive atoms. The ions thus form groups having strong internal and weak external fields of force so that these constitute molecules of considerable stability and inertness towards outside influences. The volatility of these substances and the absence of electrolytic conductivity are due to this cause.

Typical examples of complete compounds without covalence are:

Salts. — When the atomic charges are small as in NaCl, $BaBr_2$, K_2S, etc., the salts are fairly readily fusible, soluble in liquids of high dielectric constant, good electrolytic conductors when molten or in solution and very difficultly volatile. With larger charges as in MgO, BN, Al_2O_3, etc., the strong forces give great infusibility, insolubility, hardness, etc., to the substance. Such compounds are exceptionally good electric insulators at moderate temperatures but are electrolytic conductors when molten.

Silicates, glasses, slags, complex sulfides, and most minerals, etc., are compounds which usually contain several electropositive elements. In the molten, and often in the solid condition, they are electrolytic conductors and are usu-

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ally soluble in one another. The valence relation $\Sigma v_c = 0$ gives us no information in regard to the structure; for example, we can not write structural formulas for such compounds. The definite composition of many solid minerals, etc., is largely due to the regularities of the space lattices of their crystals.

Volatile halogen compounds such as AlF_3, PCl_5, SF_6, and structurally related complex ions such as SiF_6^{--} in the compound K_2SiF_6. Such high electrovalences as $+5$ for phosphorus, and $+6$ for sulfur can occur only when the tendency of Postulate 3 is counteracted by a particularly strong opposing tendency. In the case cited above it is the exceptionally great affinity of the halogen atoms for electrons that causes the action. The halogen atoms have this property in marked degree because they have larger charges on their kernels than other atoms and therefore exert a greater attraction on electrons (Coulomb's law). The fluorine atom has a greater affinity for electrons than the other halogen atoms since the radius of the atom is less and the force (by Coulomb's law) acting on the electron is greater.

b. Compounds Without Electropositive Atoms.—In these compounds the electrovalence of *every atom* must be negative, for if the electrovalence of any element is zero (inert gases) it can form no compounds. If we let v_n represent the numerical value of the negative valence we obtain from Equation (4)

$$\Sigma v_c = \Sigma v_n. \tag{6}$$

Since $v_n = s - e$, the value of v_n is fixed for any particular atom. For any given group of atoms, we can find Σv_c from (6) but we can not find the values of v_c for the individual atoms, in this way.

If, however, we place $v_c = v_n$ for each atom it is evident that Equation (6) will be satisfied. The residual charge on every atom (being $-v_n + v_c$) is then zero. Thus in any group of atoms *Postulates* 1 *and* 3 *are both completely satisfied if the covalence of each atom is equal to the negative valence of that atom*. The negative valence of carbon, nitrogen, oxygen and sulfur are 4, 3, 2 and 2 respectively, while that of hydrogen and the halogens is one. If therefore we follow the custom of the organic chemist and write structural formulas using these valences we obtain results in complete accord with Postulates 1, 2 and 3.

Thus these 3 postulates lead us to a rational derivation of the empirical valence rules which constitute the foundation of the science of organic chemistry. Moreover we are brought to see clearly the limitations of this empirical theory. We now realize that it is only *negative* valences that should be used in structural formulas (i.e., as covalences) and that even these can only legitimately be used in compounds in which electropositive atoms are entirely absent, for if some of the atoms have a positive residual charge ($v = v_e$) then from Equation (5) it is evident that other atoms must have a negative charge, and for these as well as the electropositive atoms the covalence is not equal to the negative valence.

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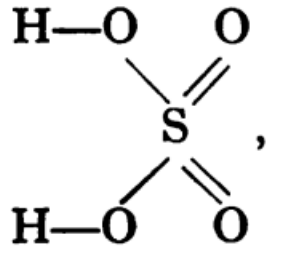
From this viewpoint it is incorrect to write structural formulas such as Na—Cl,



etc., in which the covalence of one atom is taken as equal to the positive valence of that atom.

It should be kept in mind that Postulate 3 does *not require* that v_c should be equal to v_n. There is merely a tendency for these valences to be equal. Among compounds of electropositive elements we saw that there was a conflict between the tendencies of Postulates 1 and 3 so that v was always different from zero. With compounds formed exclusively of electronegative atoms, however, there is not necessarily a conflict and it is for this reason that we have such a large class of compounds in which v is zero (i.e., $v_c = v_n$). There may be various causes that make it difficult for v to be zero even for some compounds of electronegative elements, so that in individual cases v may differ from zero by one or two units. It must be remembered that we deduced the relation $v =$ *minimum* from Postulate 3 only by assuming the two atoms which share a duplet are of substantially the same size, etc. From Coulomb's law we should expect that either a large charge on the kernel of an atom or a small radius for the kernel should cause electrons in the sheath to be held more firmly and should make it easier for the atom to acquire a negative residual charge. As an example let us consider the electronegative elements of the first two periods.

As we pass from carbon, through nitrogen and oxygen, to fluorine, the kernel charge increases and the size of the kernel presumably decreases. The residual atomic charge should thus tend to become more negative as we pass towards fluorine and more positive in comparison as we pass towards carbon. In other words, in compounds of these elements, we should expect a tendency for fluorine to have a covalence a little less than its negative valence while for nitrogen the covalence should tend to be greater than the negative valence. Since there are only eight electrons in the sheath of these atoms, the covalence of the carbon atom can never exceed four. All these conclusions are in perfect accord with experience. Thus we find the following covalences:[1]

Carbon	*4*	(3)			
Nitrogen	4	*3*	(2)		
Oxygen		(3)	*2*	1	0
Fluorine				1	*0*
Silicon	4	(or electro-positive)			
Phosphorus	*4*	3			
Sulfur	4	3	2	1	0
Chlorine	(4)	(3)	(2)	*1*	*0*

[1] See Langmuir, *J. Am. Chem. Soc.* **41**, 927 (1919).

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In this table the numbers in italics give the most common valences, while those in parentheses are only rarely found. It is clear that a large kernel charge favors covalences less than the negative valences while a small kernel charge has the opposite effect. A comparison of the elements of the second period with those of the first, shows a slight tendency for larger covalences among the heavier elements. This is to be explained as the effect of the larger kernel and hence weaker forces. There is also much more scattering among the valences of the heavier elements. This is another result of the weaker forces acting on the electrons for the covalence of such atoms is more dependent upon the electron affinity of the other atoms with which they are combined.

As an example of these relationships, let us consider the compounds, CH_4, NH_3, H_2O, and HF. In each atom of these compounds the covalence is equal to the negative valence so that the residual charge is zero and the tendencies of Postulates 1 and 3 are satisfied. If we mix the NH_3 and HF together the larger kernel charge of the fluorine as compared with the nitrogen, gives a tendency for the fluorine atom to beocme negative at the expense of the nitrogen. Thus the covalence of the fluorine decreases to zero while that of the nitrogen increases to four. This leads to the formation of the compound NH_4F which consists of NH_4^+ ions and F^- ions. The total number of covalence bonds has not been changed, they have merely been distributed differently. But this causes the atoms to become charged and makes the compound an electrolyte. It should be noted that this theory indicates definitely in what direction the change of charge occurs. Thus we should not expect NH_3 and HF to give a compound consisting of ions NH_2^- and H_2F^+ although under other conditions these ions might exist.

Similarly NH_3 and H_2O may react to form NH_4OH which will consist of ions NH_4^+ and OH^-. But the tendency to form a compound such as this is much less than in the case we have just considered, for the charge on the kernel of the oxygen atom is less than that of the fluorine atom so it has less tendency to become negative. As a result NH_3 is much less active towards H_2O than towards HF. Examples of this kind can be extended almost indefinitely and can even be used to obtain quantitative relationships between the heats of formation of various substances.

Since the sheaths of atoms of atomic number less than about 25 never contain more than 8 electrons, the covalence of these atoms can not exceed 4. With heavier atoms, however, we might expect in some cases larger covalences than 4. Large covalences are improbable in most cases for they imply equally large negative valences which means that the number of electrons in the sheath must be very much larger than the charge of the kernel. There are a few compounds, however, which suggest that large covalences sometimes exist. For example the compounds $Fe(CO)_5$ and $Ni(CO)_4$ correspond to complete compounds in which the central atoms have the covalences 10 and 8 respectively. Since e for iron is 8 and for nickel is 10 and the complete sheaths for

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these atoms contain 18 electrons, the negative valences of iron and nickel are 10 and 8, that is the same as the covalences needed to account for the above compounds. Thus these compounds are in accord with both Postulates 1 and 3, and are to be regarded as of a type analogous to organic compounds in which the covalence of *every atom* is equal to its negative valence. It should be noted that both of these compounds are liquids of low boiling point (102° and 43°) and their molecular weights have been determined. Their properties are about those to be expected if they have the structure assumed above. Other compounds of iron with carbon monoxide are known, but they have only been obtained in the crystalline state and their molecular weights are unknown.

Molybdenum carbonyl, $Mo(CO)_6$,[1] is a very easily *volatile* crystalline compound. It is interesting to note that the *negative valence* of molybdenum ($s-e = 18-6$) is twelve, so that with a covalence of 12 for the molybdenum atom in this compound we again obtain a structure consistent with the valence theory discussed above.

2. *Incomplete Compounds*

These are compounds in which some of the electrons are not arranged in complete layers or sheaths, so that the tendency of Postulate 1 is not completely satisfied. This can only occur as a result of a conflict between Postulate 1 and Coulomb's law or Postulate 3. We have seen that the tendency of Postulate 3 causes the residual charge (v) on each atom to be a minimum. The tendency of Postulate 1, however, is sufficiently strong to force the atoms to take up charges of 3, 4, or even under some conditions, 5 or 6 units, if this should be necessary in order to bring all the electrons into complete layers. Since there must be a limit to the strength of the tendency of Postulate 1 it is not surprising that residual atomic charges greater than 4 or 6 are very rare. Now the atoms of the elements near the middles of the long periods (of 18 and 32 elements), do not become complete even if they do acquire residual charges as great as 5 or 6 units, and it is therefore natural that the tendency of Postulate 3, which must become stronger as the charge increases, should prevent the formation of complete compounds of these elements. There are two types of incomplete compounds to consider.

a. Metallic Substances. Electronegative Atoms Absent.—By Coulomb's law, atoms having only small charges on their kernels, should not be able to take up enough electrons to complete sheaths of 8 or more electrons. Thus if we bring together a number of electropositive atoms there is no way in which the electrons in the incomplete sheaths can rearrange themselves to form complete sheaths. The "free" electrons which are thus compelled to remain in incomplete sheaths are responsible for the metallic properties shown by all electropositive elements in the solid or liquid state. It is clear, how-

[1] Mond, Hirtz, Cowap, *J. Chem. Soc.* **97**, 798 (1910).

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ever, notwithstanding the fact that hydrogen may sometimes function as an electropositive element, that liquid or solid hydrogen should have none of these metallic properties according to this theory, for the sheath to be formed in this case contains only two electrons. The forces acting between the free electrons and the kernels of the atoms in metallic substances, are of the same order of magnitude as in salts, so that metals have about the same range of vapor pressures, hardness, compressibilities, etc., that are shown by salts.

In general, all atoms must be electropositive unless they can take up enough electrons to complete their sheaths and thus act as electronegative atoms. The tendency of Postulate 3 ordinarily prevents the occurrence of negative valences greater than about 4. In the two short periods eight electrons are needed to form a complete sheath so that the elements with kernel charges greater than about 3 can act as electronegative atoms and therefore do not normally show metallic properties. In the 2 long periods 18 electrons form the complete sheath so that about the first 14 of the elements in each of these periods can usually act only as electropositive elements and they thus have metallic properties, when in the elementary form. For similar reasons all the known elements of the rare earth period (the last two being unknown) have metallic properties.

b. Compounds Containing Electropositive and Electronegative Atoms.— As a result of Coulomb's law or Postulate 3, the positive valence of an element is usually limited to a value of 2 or 3 unless particularly strong forces are exerted to draw away electrons, and thus raise the positive valence a few units higher. Thus in the middle of the long periods the charges of the kernels are so great that all the electrons in the sheaths of the electropositive atoms can not be given up even when other atoms are present that can take up electrons. It thus happens that the long periods contain series of elements which all have 3 or 2 and 3 as their principal valences. The atoms of these elements are therefore incomplete. The electronegative atoms in such compounds, however, are always complete.

It is of interest to note that as long as atoms are incomplete there seems to be no tendency for them to have an even rather than an odd number of electrons. For example, the following ions all have odd numbers of electrons: Cr^{+++}, Mn^{++}, Fe^{+++}, Co^{++}, and Cu^{++}. This seems to indicate that the remarkable tendency, pointed out by Lewis, for most compounds to contain even numbers of electrons is due merely to the relative abundance of complete compounds as compared to incomplete ones. In other words, the even number of electrons in most compounds results from the tendency of Postulate 1 rather than from any more general tendency for electrons to form pairs.

Many of the compounds of this class, such as ZnO (zincite), Fe_3O_4, PbS, CuO, etc., show electric conductivity even as solids. This is undoubtedly caused by the relatively large number of electrons in incomplete sheaths.

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Of course we should not expect all compounds which contain such electrons to show conductivity, for the presence of the electronegative atoms might easily prevent the mobility of these electrons. We need to know much more than we now do about the arrangement of the atoms and their electrons in space before we can predict conductivity in particular cases of this kind.

3. *Exceptional Cases*

There are some substances or compounds whose structure is not adequately accounted for by the foregoing analysis. A few examples are: N_2, CO, CN^-, NO. The writer believes these have the single octet structure which he described in his earlier publications. It is probable that acetylene, C_2H_2, and the carbide ion C_2^{--} (in CaC_2, etc.) have the same kind of structure. Pease has suggested that they may all have a triple bond structure.[1] This question merits careful study.

Another set of compounds that must have a special structure are various compounds of boron such as B_2H_6.

Most compounds containing molecules of H_2O, NH_3, etc., are readily accounted for by Postulate 3 but many of these should be considered by methods somewhat different from those developed here.

In double molecules such as H_4O_2 (in ice), H_2F_2, and in compounds such as KHF_2, etc., it seems that the hydrogen nuclei instead of forming duplets with electrons in the same atom, form duplets in which the two electrons are in different atoms. The hydrogen nucleus itself thus acts as a bond in such a case. Latimer and Rodebush[2] have made a somewhat similar suggestion in regard to hydrogen nuclei acting as bonds. They consider, however, that the hydrogen nucleus acts on two pairs of electrons: one pair in each of the two atoms. It seems to the writer much more probable that the hydrogen nucleus is no more able to attract four electrons than is the nucleus of other atoms. Since the first layer of electrons in all atoms contains only 2 electrons it seems probable that the hydrogen in this case also holds only two electrons and that these form the definite stable group which we have termed the duplet.

The writer plans to consider the quantitative aspects of these valence theories in subsequent papers. It is aimed to put Postulates 1 and 3 into a form that will permit at least rough calculations of the relative stabilities of various substances as measured, for example, by their heats of formation.

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[1] *J. Am. Chem. Soc.* **43**, 991 (1921).

[2] *J. Am. Chem. Soc.* **42**, 1431 (1920).

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PART 2

MOLECULES AND CRYSTALLINE STRUCTURE

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ISOMORPHISM, ISOSTERISM AND COVALENCE

Journal of the American Chemical Society
Vol. XLI, No. 10, 1543, October (1919).

IN RECENT papers[1] I have described a theory of valence which I have called the octet theory. This theory is based upon and is essentially an extension of G. N. Lewis' theory of the "cubical atom".[2] According to this theory each bond between adjacent atoms in organic compounds corresponds to a pair of electrons held in common by the two atoms. Since in other types of compounds the number of pairs of electrons held in common is not always the same as the number of valence bonds that have usually been assumed I proposed that the number of pairs of electrons which any given atom shares with the adjacent atoms be called the covalence of that atom. It was then shown that the covalence of carbon is always 4, that of nitrogen is usually 3 or 4, while that of oxygen is 1, 2 or sometimes 3, etc.

The octet theory indicates that the number and arrangement of electrons in the nitrogen molecule, the carbon monoxide molecule, and the cyanogen ion, is the same, and it was shown in fact that the physical properties of nitrogen and carbon monoxide are remarkably alike.

A similar relationship was found to exist between nitrous oxide and carbon dioxide and again between cyanic and hydronitric acid.

The following data, taken from Landolt-Börnstein's tables and Abegg's handbook, show the extraordinary agreement between physical properties of carbon dioxide and nitrous oxide:

	N_2O	CO_2
Critical pressure, atm	75	77
Critical temp.	35.4°	31.9°
Viscosity at 20°	148×10^{-6}	148×10^{-6}
Heat conductivity at 100°	0.0506	0.0506
Density of liquid at −20°	0.996	1.031

[1] A simpler exposition of the theory and its applications is given by Elwood Hendrick, *Met. Chem. Eng.* **21**, 73 (1919), July 15th; Langmuir, *J. Franklin Inst.* **187**, 359 (1919); *J. Am. Chem. Soc.* **41**, 868–934 (1919); *Proc. Natl. Acad. Sci.* **5**, 252 (1919).

[2] G. N. Lewis, *J. Am. Chem. Soc.* **38**, 762 (1916).

[EDITOR'S NOTE: This paper appears as Chapter Eleven in the author's book, *Phenomena Atoms and Molecules*, Philosophical Library, 1950.]

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	N_2O	CO_2
Density of liquid at +10°	0.856	0.858
Refractive index of liquid, D line, 16°	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atm, 16°	0.12×10^{-6}	0.12×10^{-6}
Solubility in water 0°	1.305	1.780
Solubility in alcohol at 15°	3.25	3.13

Both gases form hydrates, $N_2O.6H_2O$ and $CO_2.6H_2O$. The vapor pressure of the hydrate of nitrous oxide is 5 atm at −6°, whereas the hydrate of carbon dioxide has this vapor pressure at −9°. The heats of formation of the two hydrates are given, respectively, as 14,900 and 15,000 calories per mol. The surface tension of liquid nitrous oxide is 2.9 dynes per cm at 12.2°, while carbon dioxide has this same surface tension at 9.0°. Thus nitrous oxide at any given temperature has properties practically identical with those of carbon dioxide at a temperature 3° lower.

There is one property, however, which is in marked contrast to those given above. The freezing point of nitrous oxide is −102°, while that of carbon dioxide is −56°. This fact may be taken as an indication that the freezing point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of carbon dioxide is more symmetrical, and has a slightly weaker external field of force than that of nitrous oxide. Such differences could easily be produced by the difference in the charges on the kernels, and may also be taken as evidence that the structure of nitrous oxide is represented by N=N=O rather than N=O=N.

Compounds showing a relationship to one another like that between carbon dioxide and nitrous oxide will be called isosteric compounds, or isosteres. These terms, however, are not to be restricted to chemical compounds but are applicable to chemical radicals or to groups of atoms which hold pairs of electrons in common. A comolecule is defined as a group of atoms held together by pairs of electrons shared by adjacent atoms. Comolecules are thus isosteric if they contain the same number and arrangement of electrons. The comolecules of isosteres must, therefore, contain the same number of atoms. The essential differences between isosteres are confined to the charges on the nuclei of the constituent atoms. Thus in carbon dioxide the charges on the nuclei of the carbon and oxygen atoms are 6 and 8, respectively, and there are $2 \times 8 + 6 = 22$ electrons in the molecule. In nitrous oxide the number of charges on the nitrogen nuclei is 7, but the total number of electrons in the molecule is again $2 \times 7+8 = 22$. The remarkable similarity of the physical properties of these two substances proves that their electrons are arranged in the same manner.

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According to the object theory we may expect the following types of isosteres:

TABLE I

List of Isosteres

Type	
1.	H^-, He, Li^+
2.	O^{--}, F^-, Ne, Na^+, Mg^{++}, Al^{+++}
3.	S^{--}, Cl^-, A, K^+, Ca^{++}
4.	Cu^+, Zn^{++}
5.	Br^-, Kr, Rb^+, Sr^{++}
6.	Ag^+, Cd^{++}
7.	I^-, Xe, Cs^+, Ba^{++}
8.	N_2, CO, CN^-
9.	CH_4, NH_4^+
10.	CO_2, N_2O, N_3^-, CNO^-
11.	NO_3^-, CO_3^{--}
12.	NO_2^-, O_3
13.	HF, OH^-
14.	ClO_4^-, SO_4^{--}, PO_4^{---}
15.	ClO_3^-, SO_3^{--}, PO_3^{---}
16.	SO_3, PO_3^-
17.	$S_2O_6^{--}$, $P_2O_6^{----}$
18.	$S_2O_7^{--}$, $P_2O_7^{----}$
19.	SiH_4, PH_4^+
20.	MnO_4^-, CrO_4^{--}
21.	SeO_4^{--}, AsO_4^{---}

All the comolecules given under any one type are isosteric with one another.

When isosteric comolecules are also isoelectric, that is when they have the same total charge on the comolecules, all their physical properties should be closely similar. In Table I the only pairs of comolecules which are also isoelectric are: (8) N_2 and CO, (10*a*) CO_2 and N_2O, and (10*b*) N_3^- and NCO^-.

I have already pointed out that the physical properties of the first two pairs of substances (8 and 10*a*) furnish proof of the similarity of structure predicted by the octet theory, and show the usefulness of the conception of isosterism.

The isosterism of the cyanate and trinitride ions applies of course also to compounds derived from them. Thus we should expect HNCO and HN_3 to be isosteric as well as pairs of compounds such as $KNCO—KN_3$, $Ba(NCO)_2—Ba(N_3)_2$, etc.

There are, unfortunately, very few data on the physical properties of cyanates and trinitrides. Both cyanic and hydronitric acids are liquids at 0° and both explode on heating. Apparently the freezing point of cyanic acid

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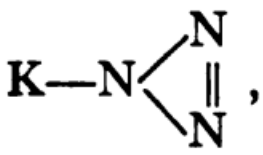
has not been determined. In a general way the solubilities of the salts of these two acids are known to be similar; the potassium and the barium salts of both acids are readily soluble in water, while the lead and silver salts are very difficultly soluble.

Groth[1] gives the following crystallographic data for anhydrous potassium cyanate and trinitride. Both belong to the tetagonal system. The ratio of the axes $a : c$ is 1 : 0.5766 for the cyanate and 1 : 0.5798 for the trinitride. Both have "strong negative double refraction". The most common faces of both crystals are given as C (001) and O (111). Cleavage was not observed in either case. No other data are given by Groth from which a comparison of cyanates and trinitrides can be made.

From the octet theory and the above data it is therefore safe to predict that the physical properties of the salts of cyanic and hydronitric acids will be found to be practically identical. This resemblance should be at least as close as that between nitrous oxide and carbon dioxide and should cover solubility in water, in alcohol, etc., density in crystalline form and in solutions, viscosity of solutions, optical and magnetic properties, electric conductivity of solutions, etc. The densities should be alike because the molecular weight of N_3 is the same as that of NCO.

The available experimental data, although meager, are sufficient, I think, to show the complete isomorphism of cyanates and trinitrides. The similarity of structure thus follows directly from Mitscherlich's rule. These experimental data furnish direct evidence against such structural formulas as


, K—N=N≡N, K—O—C≡N, but strongly support the octet theory structures

$$K^+(N{=}C{=}O)^- \text{ and } K^+(N{=}N{=}N)^-$$

These formulas show that the covalence of potassium is zero; the nitrogen and oxygen in the cyanate are dicovalent, while in the trinitride one of the nitrogens is quadricovalent and the other two are dicovalent. These data, as far as they go, thus constitute experimental proof of the octet theory of valence. Further experimental work on the physical properties of cyanates and trinitrides is highly desirable.

The octet theory also indicates that diazomethane should have the structure $H_2C{=}N{=}N$ and should thus be isosteric with $H_2C{=}C{=}O$, a compound apparently not given in Beilstein. This compound should closely resemble diazomethane in all its physical properties such as freezing point, vapor pressure, viscosity, etc.

No direct comparison can be made of the physical properties of isosteres having different electric charges. Thus we should not expect sodium salts to

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[1] P. Groth, *Chemische Krystallographie*, Leipzig, Part I, 1906, Part II, 1908.

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resemble neon, even though the sodium ion is an isostere of the neon atom—the electric force around the ion is sufficient to account for the differences in physical properties.

There is, however, another way in which the actual isosterism of comolecules with different charges can be tested from experimental data. It is evident that if any two substances are very much alike in physical properties, then any isoelectric isosteres of these substances should show similarly close relationships with one another. For example, in Types 3 and 8 of Table I, we find argon and nitrogen resemble each other closely. Therefore the chlorine ion, isosteric with argon, should have a close resemblance to the cyanogen ion which is isosteric with nitrogen. The striking similarity of chlorides and cyanides is thus directly correlated with that between argon and nitrogen.

In an exactly similar manner the close relationship between potassium salts and ammonium salts can be derived from the similarity between the physical properties of argon and methane. For from Table I (Types 3 and 9) the potassium ion is isosteric with argon, while the ammonium ion is an isostere of methane. Of course the potassium ion and the ammonium ion are not isosteres of one another. The resemblance between potassium and ammonium salts is of a much lower order than that between truly isosteric substances such as nitrous oxide and carbon dioxide, or between salts of cyanic and hydronitric acids. The octet theory indicates in fact that the potassium ion is cubic in form, while the ammonium ion, like methane, must have a tetrahedral symmetry. This conclusion is in accord with the crystal structures of potassium chloride and ammonium chloride. Bragg[1] has found that in potassium chloride each potassium ion is surrounded by 6 equidistant chlorine ions, arranged just as if the crystal were built up of cubical potassium and chlorine ions with their faces in contact; but finds that ammonium chloride, although it crystallizes in the isometric system, is in no sense isomorphous with the other alkaline halides. Each ammonium ion is surrounded by 8 equidistant chlorine ions arranged like the corners of a cube about its center. This indicates that the tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to the 4 faces or corners of the tetrahedron, while the cubical potassium ions permit the simpler cubic packing. Ammonium and potassium sulfates, however, are isomorphous, for the larger volume of the sulfate ion causes its its influence to predominate over the slight differences between the forces around the two positive ions.

The nitrates and perchlorates of all metals are readily soluble and most of them are deliquescent. From this similarity of properties we may conclude that the other isosteres of Types 11 and 14 of Table I should be interrelated.

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[1] W. H. Bragg and W. L. Bragg, *X-Rays and Crystal Structure*, London, 1916, pp. 95 and 158.

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Thus carbonates and sulfates should show a general resemblance to each other in their solubilities.

The smaller solubility of salts of divalent ions is, of course, due to the greater forces holding the divalent ions, making it more difficult for them to separate. The process of solution of salts involves, according to the octet theory, the separation of the ions. Thus sulfates and carbonates of most metals are difficultly soluble compared to the nitrates and perchlorates. Salts like lead and barium carbonates and sulfates in which both ions are divalent, are thus particularly difficultly soluble.

Boron nitride, which consists of tervalent ions, has still greater stability, and is infusible and insoluble in all solvents.

The observed differences between the ordinary properties of the differently charged isosteres are thus to be expected. But there is one property, namely crystalline form, which should depend on the arrangement of the electrons in substances rather than upon the magnitude of the forces between their atoms. By a comparison of crystal forms it should therefore be possible to obtain direct evidence of the similarity of the arrangement of the electrons in isosteric substances even if the charges on the comolecules are different.

For example, since the sodium ion and the fluorine ion are isosteric and cubic in form, we should expect them to pack together in a crystal lattice in exactly the way that Bragg has found they do. The magnesium and oxygen ions, however, are also isosteric with the sodium and fluorine ions, so that we should expect magnesium oxide to have a crystal structure identical in form with that of sodium fluoride. According to Groth both substances are cubic, sometimes crystallizing as octahedra, and both show good cleavage parallel to the (100) plane. To answer the question thus raised, Dr. A. W. Hull has studied the X-ray patterns obtained with magnesium oxide and sodium fluoride and has thus recently found[1] that the crystal structures of substances are alike, except that the atoms in magnesium oxide are drawn closer together by the greater forces. Thus magnesium oxide and sodium fluoride should be looked upon as isomorphous. By the octet theory the covalences of all the atoms in these substances are zero, since they do not share electrons with each other. The isomorphism is thus in full accord with Mitscherlich's rule by which isomorphous substances should have similar structures. Since the ions O^{--}, F^{-}, Na^{+} and Mg^{++} are isosteric we should also expect that MgF_2 and Na_2O should be isomorphous. Groth states that sodium oxide has not been obtained in the form of well developed crystals. However, by Hull's method of X-ray analysis, substances can now be studied in powdered form so that we may hope to see whether in fact these two substances are isomorphous. Other pairs of substances which may be isomorphous are

[1] Soon to be published.

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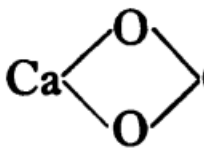
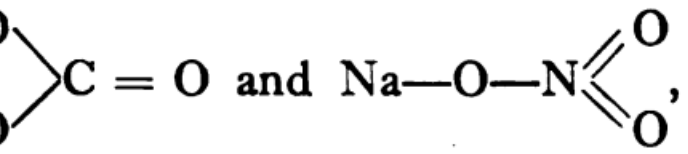
potassium chloride and calcium sulfide, potassium sulfide and calcium chloride, cuprous sulfide and zinc chloride, etc.

A still more interesting class of isomorphous substances which are predicted by the octet theory is that represented by sodium nitrate and calcium carbonate. Since the nitrate and carbonate ions are isosteric we should expect sodium nitrate and magnesium carbonate to be isomorphous, Na^+ and Mg^{++} being isosteric. As a matter of fact, both substances are given by Groth as trigonal scalenohedral with the ratio of the axes 1 : 0.8297 and 1 : 0.8095, respectively.

The practical identity in all the crystallographic properties of sodium nitrate and calcium carbonate has long been known. In Mitscherlich's early theory before clear ideas of valence were developed, no difficulty was experienced in regarding these two substances as isomorphous and as having similar structures. The theory of valence, however, gave formulas  and  , so that they could no longer be regarded as of similar structure. It was necessary either to abandon Mitscherlich's rule or to re-define isomorphism so as to exclude cases of this kind. Therefore Kopp[1] and Retgers[2] regarded substances as isomorphous only when they are capable of forming *mixed crystals*. This effectually eliminated such cases as sodium nitrate and calcium carbonate because mixed crystals can naturally only be obtained when the solubilities of the two substances are not too widely different. The crystal form depends, of course, exclusively, on the arrangement of the atoms and the electrons in them, while the ability to form mixed crystals depends on both similarity of arrangement and on similarity in the magnitude of the forces acting between the atoms. Thus Kopp found a practical rule by which nearly all those cases inconsistent with the ordinary valence theory, could be excluded. In order to be isomorphous in Kopp's sense, two substances must have atoms which are not only linked together in the same manner, but also have the same number of available electrons in corresponding atoms.

T. V. Barker,[3] however, and a few others crystallographers have maintained that isomorphism should be used to denote similarity of crystal form. Barker pointed out a great many new cases of isomorphism between substances which according to the ordinary valence theory are not closely related. Among these he mentions as types KIO_4-CaWO_4; $KClO_4-BaSO_4-KBF_4$; $K_2SO_4-K_2BeF_4$; and $NaNO_3-CaCO_3$. He shows how these cases of isomorphism are inconsistent with the ordinary valence theory, but are in a general way in agreement with Werner's co-ordination theory.

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[1] *Ber.* **12**, 868 (1879).

[2] *Z. physik. Chem.* **3**, 497 (1889), and later papers in 1889 to 1896.

[3] *Trans. Chem. Soc.* **101**, 2484 (1912).

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By examining Table I it is evident that we should expect the following cases of isomorphism of the kind just considered:

TABLE II

Typical Cases of Isomorphism Based on Isosterism

Type Table I	
2.	(*a*) $NaF-MgO$; (*b*) MgF_2-Na_2O
3.	(*a*) $KCl-CaS$; (*b*) $CaCl_2-K_2S$
5.	(*a*) $RbBr-SrSe$; (*c*) $SrBr_2-Rb_2Se$
7.	(*a*) $CsI-BaTe$; (*c*) BaI_2-Cs_2Te
8.	N_2-CO
10.	$KNCO-KN_3$, etc.
11.	(*a*) $NaNO_3-CaCO_3$; (*b*) KNO_3-SrCO_3
14.	(*a*) $KClO_4-SrSO_4$; (*b*) $NaHSO_4-CaHPO_4$
	(*c*) $KHSO_4-SRHPO_4$
15.	(*a*) $NaClO_3-CaSO_3$; (*b*) $KHSO_3-SrHPO_3$
17.	$Na_2S_2O_6-Ca_2P_2O_6$
18.	$Na_2S_2O_7-Ca_2P_2O_7$
20.	$RbMnO_4-BaCrO_4$
21.	$MnSeO_4.2H_2O-FeAsO_4.2H_2O$

Sodium nitrate crystals resemble those of calcium carbonate a little more closely than those of magnesium carbonate, although the sodium ion is isometric with the magnesium ion but not with the calcium ion. The molecular volume of sodium nitrate is nearer to that of calcium carbonate than that of the magnesium compound. The much larger forces in the compounds containing the divalent ions must tend to draw the atoms together. The substitution of the larger calcium ion in place of the magnesium ion offsets this difference, and this probably accounts for the closer resemblance between the sodium and the calcium compounds. This same relationship is noticed in other pairs of compounds. Since in these replacements calcium corresponds most nearly to sodium we should expect stronium to correspond to potassium and barium to rubidium. This is well borne out in every case. The following tables illustrate the cases of isomorphism corresponding to Types 11 to 21, shown in Table II, for which data are given by Groth. The pairs of substances at the head of each table are those given in Table II. The other substances are generally recognized as being isomorphous with one or the other member of these pairs.

Groth gives no data for the Types 15(*a*), 15(*b*), 17 and 18 of Table II.

The results given in these tables afford the strongest kind of evidence for the octet theory of valence and prove that crystal form depends on the covalence of the atoms forming the substance rather than upon the valences given by the ordinary theory.

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In every one of the cases where isomorphism is predicted by the octet theory (see Table II), we find that the data available in Groth's "Chemische Kristallographie" indicate an almost complete identity of crystalline form.

TABLE III

Nitrates and Carbonates Type 11 (*a*). *Trigonal Scalenohedral*

	a : *c*	
$NaNO_3$	I : 0.8297	
$CaCO_3$	I : 0.8543	
$MgCO_3$	I : 0.8095	
$MnCO_3$	I : 0.8259	
KNO_3	I : 0.8259	Stable above 128°

At high temperatures $RbNO_3$, $SrCO_3$ and $BaCO_3$ also give trigonal crystals.
All these substances show strong negative double refraction and similar cleavage.

TABLE IV

Nitrates and Carbonates, Type 11 (*b*). *Orthorhombic Bipyramidal*

	a	:	*b*	:	*c*
KNO_3	0.5910	:	I	:	0.7011
$SrCO_3$	0.6090	:	I	:	0.7237
$CaCO_3$	0.6228	:	I	:	0.7204
$BaCO_3$	0.5949	:	I	:	0.7413

Negative double refrection.

TABLE V

Perchlorates and Sulfates, Type 14 (*a*) *Permanganates and Chromates, Type* 20. *Orthorhombic Bipyramidal*

	a	:	*b*	:	*c*		Cleavage
$KClO_4$	0.7817	:	I	:	1.2793	*c*(001)	*m*(110)[1]
$SrSO_4$	0.7790	:	I	:	1.2800	*c*(001)	*m*(110)[1]
$RbMnO_4$	0.8311	:	I	:	1.3323	..	....
$BaCrO_4$	0.8231	:	I	:	1.3232	..	....
$RbClO_4$	0.7966	:	I	:	1.2879	*c*(001)	*m*(110)
$BaSO_4$	0.8152	:	I	:	1.3136	*c*(001)	*m*(110)[1]
$KMnO_4$	0.7972	:	I	:	1.2982	*c*(001)	*m*(110)[1]
$SrCrO_4$	0.9496	:	I	:	1.0352	..	....
$CsClO_4$	0.8173	:	I	:	1.2976	..	....
$CsMnO_4$	0.8683	:	I	:	1.3705	..	....
$CaSO_4$	0.8932	:	I	:	1.0008	..	....
NH_4ClO_4	0.7932	:	I	:	1.2808	.. .	....

[1] Incomplete cleavage.

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TABLE VI

Sulfates and Phosphates, Type 14 (*b*). *Triclinic Pinacoid*

	a	*b*	*c*	*α*	*β*	*γ*
$NaHSO_4$[2]	0.6460	I	0.8346	85° 06′	88° 57′	86° 47′
$CaHPO_4$	0.6467	I	0.8244	84° 57′	89° 43′	85° 38′
$SrHAsO_4$	0.6466	I	0.8346	86° 32′	89° 14′	87° 56′

TABLE VII

Sulfates and Phosphates, Type 14 (*c*). *Orthorhombic Bipyramidal*

	a	*b*	*c*
$SrHPO_4$[1]	0.8581	I	1.9431
$KHSO_4$	0.8609	I	1.9344

Both substances form 8- or 4-sided plates parallel to *c*(001) with (111) as the next most important face. The plane of the optic axis is (001).

TABLE VIII

Selenates and Arsenates, Type 21. *Orthorhombic Bipyramidal*

	a	*b*	*c*
$MnSeO_4.2H_2O$	0.8849	I	0.9959
$FeAsO_4.2H_2O$	0.8658	I	0.9541

Plane of the optic axis (100) in both.

[1] Axes *b* and *c* have been interchanged in order to correspond to those used to form the other compounds. Where the angles *α*, *β*, *γ*, were greater than 90° their supplementary angles were chosen.

[2] The measurements on $SrHPO_4$ and on $CaHPO_4$ given in Table VI were made by Schulten *Bull. Soc. franç mineral* **27**, 120 (1904).

According to Groth the ratio of the axes for $SrHPO_4$ was found to be 0.6477:1:0.8581 and the only faces measured were (100), (133), (203), (130), (230), (010). Groth states that the chosen orientation of the $CaHPO_4$ crystals was adopted because of the relationships to those of $SrHPO_4$.

For the substance $BaHPO_4$ which Schulten finds to be orthorhombic he gives the ratios 0.7133 :1:0.8117, and considers that these ratios are related to those given above for $SrHPO_4$ (see Groth, p. 815) although the crystals are of "entirely different form." These facts make it clear that Schulten chose for this orthorhombic crystal the axial ratio *a*:*b*::0.6477:1 simply to make this ratio agree with *a*:*b*::0.6467:1 which he had obtained for the *triclinic* crystals of $CaHPO_4$ and which he supposed isomorphous with $SrHPO_4$ notwithstanding that they belonged to a different crystal system. If we multiply the *a* intercept 0.6477 by 3 and then interchange the *a* and *c* axes we obtain the ratios given above in Table VII. The crystal faces which Schulten measured should thus be denoted by (100), (111), (201), (110), (210), and (010) instead of the absurd set of faces (100), (133), (203), (130), (230) and (010) given by Schulten. There is thus ample internal evidence for making this change in Schulten's data. We may conclude that there is no similarity in the ratios between the axes of the triclinic $CaHPO_4$, the orthorhombic $SrHPO_4$ and the orthorhombic $BaHPO_4$, but they represent 3 distinctly different crystal types.

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The agreement between the pairs of substances given in Table II is in fact usually rather better than among most of the classical examples of isomorphism. For example, the agreement of the ratios of the axes for potassium perchlorate and strontium sulfate (Table V) is much closer than among the various chlorates or among the sulfates. Sodium nitrate crystals (Table III) are more nearly like calcium carbonate than these are like magnesium carbonate. Potassium nitrate (Table IV) shows better agreement with strontium carbonate than calcium carbonate (aragonite) does with barium carbonate. Sodium hydrogen sulfate (Table VI) agrees slightly better (in axial angles) with calcium hydrogen phosphate than this does with strontium hydrogen arsenate.

In several of the cases in Table II we find that no data are given by Groth by which a comparison between the crystalline form of similarly constituted compounds can be made. For example (Type 15*a*), no anhydrous sulfites of divalent metals and no hydrated chlorates of univalent metals are given. Although sodium hydrogen sulfite is given, no phosphites of divalent metals have been measured.

It seems safe to predict that nearly all the remaining pairs of substances given in Table II will be found to be isomorphous when data become available. By Hull's method of X-ray analysis these comparisons are now possible even with powdered materials, so that most of the difficulties disappear that have heretofore prevented the accumulation of such data.

We have thus far considered cases in which the octet theory leads us to expect isomorphism not predicted by the ordinary theory of valence. Let us now consider those cases where the ordinatry theory indicates isomorphism, but the octet theory does not. Examples of this kind are, (*a*) carbonates and sulfites, (*b*) chlorates and nitrates, (*c*) chlorates and metaphosphates.

According to the ordinary theory the sulfur in sulfites has a valence of 4 like that of carbon in carbonates. In chlorates and nitrates the central atom is supposed to have a valence of 5. By the octet theory, however, the covalence of sulfur in normal sulfites is 3, while that of carbon in carbonates is 4. In chlorates the covalence of chlorine is 3, while in metaphosphates that of the phosphorus is 4. A great deal of effort has been expended by chemists and crystallographers to prove cases of isomorphism between nitrates and chlorates. Groth says that carbonates and sulfites should be expected to be isomorphous and recommends that much more work be done in a comparative study of these salts—especially he advises attempting to prepare mixed crystals. In spite of this effort and the belief of chemists in the similarity of the constitutions of these compounds, there seem to be no convincing data indicating similarity of crystalline form in these cases. For example, Groth points out that potassium hydrogen carbonate and potassium hydrogen sulfite both belong to the monoclinic system, and that their crystals have the same habit. An examination of the data shows that both form crystals

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which are elongated in the direction of the *b*-axis. The following crystallographic data, however, prove that the substances are very far from isomorphous:

	a	*b*	*c*	*β*
$KHCO_3$	2.6770	I	1.3115	103° 25′
$NaHCO_3$	0.7645	I	0.3582	93° 19′
$KHSO_3$	0.9276	I	2.2917	94° 46′

The ratios of the axes could hardly be more different, and there is a difference of 9° in the inclination of the axes. The sodium acid carbonate is also monoclinic but has quite different constants from either of the other compounds. No other anhydrous sulfites are given by Groth.

The following hydrated sulfites and carbonates given by Groth are the only ones that are comparable in constitution. Ammonium sulfite, $(NH_4)_2SO_3.H_2O$, is monoclinic while sodium carbonate, $Na_2CO_3.H_2O$, is orthorhombic. The compound $Na_2CO_3.7H_2O$ is orthorhombic but $Na_2SO_3.7H_2O$ is monoclinic. Finally, $MgCO_3.3H_2O$ crystallized in the orthorhombic system, while $MgSO_3.3H_2O$ is "ditrigonal pyramidal." All of the available crystallographic data thus seem to indicate conclusively that sulfites and carbonates do not have similar constitutions.

The chlorates and nitrates usually have different crystalline forms, but in many cases it has been found possible to make mixed crystals containing as much as 10 or 15% of one or the other of the constituents. Sodium chlorate crystallizes in the cubic system isomorphous with sodium bromate, while sodium nitrate is trigonal. This form of sodium chlorate is normally produced either from aqueous solution or by cooling the molten mass. By slow evaporation of a strongly supersaturated aqueous solution it is possible to obtain sodium chlorate in a trigonal form with angles very much like those of sodium nitrate, and also having negative double refraction like that of sodium nitrate; this trigonal form of sodium chlorate is very unstable, and soon goes over into the cubic form even at room temperature. It was found possible to prepare mixed crystals of sodium nitrate and chlorate containing as much as 22.5% of the chlorate. An unstable monoclinic form of sodium chlorate has also been prepared.

Potassium chlorate crystallizes only in the monoclinic form with axes inclined 109°, while potassium nitrate is orthorhombic. Notwithstanding the fact that the crystals belong to different systems, Groth states that potassium chlorate and sodium nitrate closely resemble each other. He does not believe that mixed crystals can be formed because the molecular volumes are so different. However, monoclinic mixed crystals of potassium chlorate and potassium nitrate up to 15 % of the nitrate have been obtained, as well as orthorhombic mixed crystals, with 25 % of the chlorate. This is considered to denote

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similarity of structure, notwithstanding the complete difference of crystal form between potassium nitrate and chlorate. Silver chlorate and bromate are tetragonal while silver nitrate is orthorhombic. The chlorate also forms cubic crystals isomorphous with sodium chlorate. Silver chlorate thus shows no resemblance to the nitrates.

Anhydrous calcium, strontium, and barium nitrates crystallize in the cubic system, but strontium chlorate $Sr(ClO_3)_2$ is orthorhombic with axial ratios, 0.9174:1:0.6003. It also exists in 3 other modifications, no one of which is cubic. However, even here it has been possible to make mixed crystals containing 7 to 12 % of chlorate.

The salts $Mg(NO_3)_2.6H2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, are monoclinic, the nickel and cobalt salts being isomorphous with each other but not with the magnesium salt. On the other hand, the corresponding chlorates of nickel and cobalt, $Ni(ClO_3)_2.6H_2O$, etc., and the bromates of magnesium, nickel, cobalt and zinc, $Mg(BrO_3)_2.6H_2O$, etc., are cubic. Only in one instance were mixed crystals obtained: $Zn(BrO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ crystallizing together as cubic crystals.

Looking back over this comparison of chlorates and nitrates we see that among the 20 compounds considered (belonging to 5 different crystal systems), there is only one instance, namely that of sodium nitrate and the unstable trigonal modification of sodium chlorate, in which corresponding nitrates and chlorates even belong to the same system.

This evidence seems sufficient to prove that nitrates and chlorates have fundamentally different constitutions. A careful study of the trigonal form of sodium chlorate should be made, preferably by the X-ray method, to determine if its structure is actually like that of sodium nitrate. If it turns out to be so, it is probably to be explained as a very unusual form in which two of the electrons in the atoms constituting the chlorate ion become unavailable, perhaps by being imprisoned within one of the octets. Under such conditions the chlorate ion might become "pseudo-isosteric" with the nitrate ion, so that the chlorine atom might then act with a covalency of 4.

There are no available data by which to test isomorphism between chlorates and metaphosphates.

These considerations show that the ordinary valence theory not only fails to predict cases of isomorphism which do exist (for example, potassium chlorate and strontium sulfate) but predicts isomorphism (sulfites and carbonates) where none exists. The octet theory does not fail in either of these ways. I have used the word isomorphism as expressing a close resemblance in crystallographic data. The data given in the cases of the nitrates and chlorates show conclusively in my mind that the formation of mixed crystals often occurs when there is no close resemblance in crystal structure. It seems therefore that this criterion should not be used to indicate similarity in chemical constitution. The question of course arises: how many other cases of mixed crystals

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could be found if the same effort were expended in looking for them among other types of compounds.

Let us now consider in more detail the cases of isomorphism given by Barker:

	a	*b*	*c*	*β*
A. Monoclinic				
$CuTiF_6.4H_2O$	0.7471	I	0.5564	104° 9′
$CuCbOF_5.4H_2O$	0.7627	I	0.5629	103° 20′
$CuWO_2F_4.4H_2O$	0.7648	I	0.5629	103° 14′
B. Monoclinic				
K_3HSnF_8	0.6277	I	0.4928	93°
K_2HCbOF_7	0.6279	I	0.4900	93° 14′
C. Orthorhombic				
$K_2SnCl_4.2H_2O$	0.6852	I	0.7586	....
$K_2FeCl_5.H_2O$	0.6911	I	0.7178	....
D. Monoclinic				
$MnCl_2.4H_2O$	1.1525	I	0.6445	99° 25′
$BeNa_2F_4$	0.9913	I	0.6929	99° 20′
E. Tetragonal				
YPO_4	..	I	0.6177	....
$ZrSiO_4$	..	I	0.640	....
Sn_2O_4	..	I	0.6726	....
F. Tetragonal				
KIO_4	..	I	1.5534	....
$CaWO_4$	..	I	1.5268	....
$KOsO_3N$	..	I	1.6319	....
$KRuO_4$	..	I	1.6340	....
G. Orthorhombic				
$KClO_4$	0.7817	I	1.2792	....
$BaSO_4$	0.8152	I	1.3136	....
KBF_4	0.7898	I	1.2830	....
H. Orthorhombic				
K_2SO_4	0.5727	I	0.7418	....
K_2BeF_4	0.5708	I	0.7395	....
$[N(CH_3)_4]2HgCl_4$	0.5766	I	0.7893	....
$ZnI_2.4NH_3$	0.5754	I	0.7922	....
I. Monoclinic				
$(NH_4)_2SeO_4$	1.8900	I	1.1987	115° 29′
Cs_2HgI_4	1.3155	I	0.9260	110° 4′
(the cleavage is the same)				
J. Trigonal				
$NaNO_3$	..	I	0.8297	....
$CaCO_3$	..	I	0.854	....
K.				
Albite $NaAlSi_3O_8$ } Are closely isomorphous				
Anorthite $CaAl_2Si_2O_8$ }				

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The theory of chemical structure given in the recent paper in *J. Am. Chem. Soc.* **41,** 868 (1919) is in full accord with these cases of isomorphism, and affords an explanation of them. In the second method[1] of regarding complex compounds with a co-ordination number of 6 or more, it was explained how groups such as chloride ion, ammonia, water, etc., could be held by electrostatic attraction to a positively charged central atom. We have already seen how in typical octet compounds such as potassium sulfate, etc., oxygen is unicovalent and may thus be replaced by fluorine without involving a change in the crystalline structure. The compounds in Groups A, B, G, and I are examples of this kind where fluorine, iodine or oxygen replace one another. Group C gives an illustration of a positive central ion (Sn^{++} or Fe^{+++}) surrounded by 6 other groups (Cl^- or H_2O) forming a complex ion. The H_2O group in the first compound replaces one of the chlorine ions of the second.

The compounds of Groups D and H afford interesting illustrations of the replacement of negative by positive ions and *vice versa* in a manner exactly analogous to that of NA_2O-MgF_2, etc., of Table II. Thus in $BeNAF_4$ the two sodium ions replace the two chlorine ions of the $MnCl_2-4H_2O$, the beryllium ion replaces the manganese ion and the fluorine ions replace the water comolecules. Similarly, in comparing $ZnI_2.4NH_3$ with K_2SO_4 we see that the iodide ions have replaced the potassium ions. This is evident if we apply the octet theory in the ordinary way to the compound $ZnI_2.NH_3$. The number of available electrons in the atoms of this compound is $e = 48$. We place $n = 7$, assuming that the zinc, iodine and nitrogen atoms all form octets. We then find from the octet equation ($2p = 8n - e$) the value $p = 4$, from which we find the structure $I_2^-[Zn(NH_3)_4]^{++}$, in which each nitrogen a tom isquadricovalent and shares a single pair of electrons with the octet of the zinc atom. The constitution is thus exactly analogous to $K_2^+SO_4^{--}$, for in this case the quadricovalent sulfur atom shares a single pair of electrons with each of the oxygen atoms.

If we apply the octet theory in the same way to $BeNa_2F_4$ and $MnCl_2.4H_2O$ we place for both compounds $e = 32$, $n = 5$ and find $p = 4$. This gives the structures

$$[Mn(OH_2)_4]^{++}Cl_2^- \quad \text{and} \quad [BeF_4]^{--}Na_2^+.$$

The manganese and beryllium atoms are thus quadricovalent, the water and iron share single pairs of electrons with the central atom. In the first compound the oxygen is tercovalent. The substitution of water or ammonia for fluorine or oxygen in these compounds is analogous to the substitution of K^+ in K_2SO_4 by NH_4^+.

The same explanation apply to the other examples cited by Barker. Those shown in Group K are of interest because in silicates we usually have to

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[1] *J. Am. Chem. Soc.* **41,** 868 (1919) beginning middle of p. 930.

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deal with compounds in which no pairs of electrons are held in common between atoms. Thus in the octet equation $2p = 8n - e$ we place $p = 0$ and find $e = 8n$. In silicates, oxygen is the only element which forms octets, so n is equal to the number of oxygen atoms. This condition ($e = 8n$) is practically the only valence condition that needs to be fulfilled by silicates, and it is thus a complete statement of the valence theory for these compounds. The isomorphism of the two compounds of Group K is consistent with the octet theory since in both compounds the number of atoms is alike (13) and so is also the number of available electrons, $e = 8n = 64$.

Summary

The octet theory of valence indicates that if compounds having the same number of atoms have also same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule.

Table I gives a list of various isosteres predicted by the octet theory. For example, O^{--}; F^-; Ne, Na^+ and Mg^{++} are isosteric. Other examples are N_2—CO—CN^-; CH_4—NH_4^+; N_4^-—CNO^-; ClO_4^-—SO_4^{--}—PO_4^{---}; NO_3^-——CO_3^-, etc. In cases where isosteric groups have the same electric charges (isoelectric) their properties are directly comparable; thus N_2 and CO; N_2O and CO_2; KN_3 and KNCO, etc., are nearly alike (in pairs) in all their physical properties. But when the charges are unlike the similarity may manifest itself between properly chosen compounds; thus, according to the theory, we should expect sodium nitrate and calcium carbonate to have similar constitutions and therefore to have similar crystalline forms, as is in fact known to be the case.

The following cases of crystalline isomorphism are thus predicted by the theory and are found to exist according to published crystallographic data: NaF—MgO; KN_3—KNCO; KNO_3—$SrCO_3$; $KClO_4$—$SrSO_4$; $NAHSO_4$—$CaHPO_4$; $MnSeO_4.2H_2O$—$FeAsO_4.2H_2O$, etc. The following cases are predicted by the theory but cannot yet be tested because of lack of available data: MgF_2—Na_2O; K_2S—$CaCl_2$; $NaClO_3$—$CaSO_3$; $KHSO_3$——$SrHPO_3$; $Na_2S_2O_6$—$Ca_2P_2O_6$; $Ca_2S_2O_7$—$Ca_2P_2O_7$; etc.

The theory of isosterism makes it possible to derive certain relationships in a very simple manner. Thus since argon is an isostere of the potassium ion and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relation between argon and nitrogen enables us to trace an equally close relationship between the cyanogen and the chlorine ions. From the similarity in the

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solubilities of nitrates and perchlorates we may also conclude that carbonates and sulfates should be closely related.

The experimental data discussed prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. In particular, the experimental results justify the following conclusions:

1. The covalence of sodium, potassium, chlorine in chlorides, is zero.

2. The covalence of the central atom is 4 in nitrates, carbonates, sulfates, perchlorates, phosphates, permanganates, chromates, selenates, arsenates, borofluorides, etc.

3. Carbonates and sulfites are not isomorphous, the covalence of the central atom being 4 and 3, respectively.

4. Nitrates and chlorates are not isomorphous, the covalency of the chlorine being 3 in chlorates.

5. The applicability of the octet theory to complex inorganic compounds receives further confirmation by its ability to explain such cases of isomorphism as between Na_2BeF_4 and $MnCl_2.4H_2O$; K_2SO_4 and $ZnI_2.4NH_3$, $K_2SnCl_4.2H_2O$ and $K_2FeCl_5.H_2O$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$, etc.

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THE STRUCTURES OF THE HYDROGEN MOLECULE AND THE HYDROGEN ION

Science
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IN A LETTER to *Science* published June 18 I described a model for the helium atom which is in better accord with the chemical relationships of helium than is the model proposed by Bohr. It leads to a value 25.59 volts for the ionizing potential in agreement with experimental determinations while Bohr's theory gives too high a value. In the model which I proposed the two electrons move in separate orbits in a plane containing the nucleus. The electrons are always symmetrically located with respect to a second plane which passes through the nucleus and is pependicular to the plane of the orbits. Each electron thus oscillates back and forth along an approximately semi-circular path.

We may conceive of the hydrogen molecule as having a similar structure except that there are two nuclei. The electrons may thus move in separate orbits in a plane which is perpendicular to and bisects the line connecting the nuclei. The positions of the electrons at any time are symmetrical with respect to another plane which passes through both nuclei. Starting from two points on opposite sides of the center of the molecule, we may imagine the electrons to revolve about the center in opposite directions. After something less than a quarter revolution the electrons come so close to one another that the repulsive forces between them bring them both to rest. These forces then cause them to return back along the same paths to the starting points. They then continue their motion and complete another quarter of a cycle before they again come to rest. Each electron thus oscillates along a nearly semicircular line.

On the basis of the classical mechanics, by a series of approximations, it is possible to calculate the size and shape of the orbits and the relative velocities of the electrons at any point in their paths in terms of the distance between the nuclei. If we let a be the distance from the center of the molecule to the mid-point of the nearly semicurcular orbit of the electron, then the distance between the nuclei is $0.619 \times a$ and the radius vector of the electron at the ends of the orbit (where the electron comes to rest) is $1.152 \times a$. The angle through which the electrons move is 71°26′ each side of the mid-point as measured from the center of the molecule. The angular velocity of the electrons at the mid-points of their paths is such that if they continued to move

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with this velocity they would travel through 106° 00′ during the time that they actually take to move to the end of the orbits (i.e., through 71° 26′). The total energy (W) of the molecule (kinetic plus potential) is found to be $1.604\, W_0 a_0/a$ where W_0 is the corresponding energy for the hydrogen atom according to Bohr's theory and a_0 is the radius of the electron orbit in the hydrogen atom (0.530×10^{-8} cm).

It should be possible by means of the quantum theory to determine a, and fix the absolute dimensions of this model. But, so far as I know, the quantum theory has not yet been formulated in such a way that it can be applied with certainty to the type of motion that we are here considering. The quantum condition $fpdq = nh$ is only valid when the co-ordinates are chosen in a particular manner, and for a case like the one in hand I have not been able to find any general method for determining what system of co-ordinates should be used. It may be, however, that others having greater familiarity with the recent mathematical development of the quantum theory will be able to determine the value of a for the model under consideration.

I have therefore proceeded to calculate the value of a from the known heat of dissociation of molecular hydrogen into atoms, and then to test this result by calculating other properties of hydrogen. Taking q the heat of dissociation (at constant volume), as 84,000 calories per gram molecule we find that $W/W = 2.270$. Since q is proportional to $W-2W_0$ it takes a relatively large change in q to have much effect on the value of W. Thus an error of eight per cent in determining the heat of dissociation (which is greater than the probable error), would cause only a one per cent error in W and in a. From the relation previously given, we thus find $a = 0.707a_0 = 0.375\times10^{-8}$ cm. When the electrons are at the ends of their orbits their distance from the center is 0.432×10^{-8} cm. In Bohr's model for the hydrogen molecule the radius of the orbit of the electrons is $0.953\ a_0$ or 0.506×10^{-8} cm. In the new model the distance of the nuclei from the center is 0.232×10^{-8} cm while in Bohr's model this distance is 0.292×10^{-8} cm. The moment of inertia of the molecule about its center is thus 1.78×10^{-41} g cm² for the new model while Bohr's model gives $2.81\times^{-41}$ g cm². From the theory of band spectra which has recently been developed by Lenz, Heurlinger and others it is possible to calculate the moment of inertia of the hydrogen molecule from certain relationships between lines of the secondary spectrum of hydrogen which were found by Fulcher and Croze. Thus Sommerfeld[1] calculates that the moment of inertia of the hydrogen molecule is 1.85×10^{-41}. This value agrees within four per cent with that calculated from the new model (1.78×10^{-41}) while Bohr's model gives a value 52 per cent too high.

It is of interest to enquire if there are not other simple models for the hydrogen molecule which are consistent with the known chemical facts regard-

[1] *Atombau und Spectrallinien*, p. 561, 2nd edition, soon to be published.

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ing the remarkable stability of a pair of electrons in molecules. Sommerfeld has modified Bohr's original theory of atomic structure by considering elliptical as well as circular orbits. A two-quantum orbit of an electron in an atom may have both quanta in the form of angular momentum (circular orbit), or there may be one quantum of angular and one of radical momentum (elliptical orbit). Both quanta can not be in the form of radial momentum, for the ellipse would then degenerate into a straight line which would pass through the nucleus and this would lead to infinite velocities for the electron. This reason for the exclusion of orbits having only radial quanta fails for the case of a molecule in which there is no nucleus at the center. We should therefore consider models for the hydrogen molecule in which the two electrons oscillate in and out along a straight line passing through the center of the molecule, and perpendicular to the line joining the two nuclei. The repulsion of the electrons for each other would prevent them from reaching the center. We assume of course that the two electrons are coupled together by some quantum relationship, in such a way that they are always at equal distances from the center. If the electrons are at their greatest distance from the center they are more strongly attracted by the two nuclei than they are repelled from each other and they therefore fall in towards the center. When they get close to the center the repulsion increases rapidly and finally causes the electrons to rebound to their original positions. When the electrons are far apart there is a net repulsive force between the nuclei, but when the electrons are close together the attractive force on the nuclei predominates. The length of the path traveled by the electrons must be so related to the distance between the nuclei that the time averages of the repulsive and attractive forces acting on the nuclei must be equal.

By a series of approximations, based wholly on the classical mechanics, the following results have been calculated. If we take b, the distance between the center of the molecule and the nuclei as unity, the maximum distance reached by the electrons (from the center) is 3.710, while the minimum distance within which they approach the center is 0.1644. The electrons attain their greatest velocity when they are at a distance of 0.5773 from the center, and if they continued to move with this velocity they would travel a distance 8.989 in the time that it actually takes to move from the position of nearest approach to the point in the orbit furthest from the center. The total energy W of the molecule according to this model is $0.8124\ W_0 a_0/b$ where W_0 and a_0 have the same meanings as before.

In the absence of definite knowledge as to how to apply the quantum theory to this model we may calculate the absolute dimensions from the heat of dissociation. Taking as before $W = 2.270\ W_0$ we find for b, the distance from the nuclei to the center of the molecule, the value 0.190×10^{-8} cm. The moment of inertia is thus 1.20×10^{-41} g cm^2. Since this value does not agree at all well with the value 1.85×10^{-41} calculated from the spectrum it is improbable that

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this model corresponds to the true structure of the hydrogen molecule in its normal state. It may be however that such a model with a different value for b may apply to a disturbed state of the molecule.

According to Bohr's theory in which the paths of electrons are circular, a hydrogen ion consisting of two hydrogen nuclei with one electron, should not be capable of existing, for the value of W for such a structure ($0.88\ W_0$) is less than that for the hydrogen atom and the ion should therefore break up into an electron and a hydrogen atom. There seems to be considerable experimental evidence[1] that the positive H_2 ion is stable and is formed from ordinary molecular hydrogen when an ionizing voltage of about 11 volts is applied.

Since the H_2^+ ion has two nuclei there is no obvious necessity for assuming a circular path for the electron. I have therefore considered a model in which the electron oscillates along a rectilinear path passing through the center of the ion and perpendicular to the line joining the nuclei. By the methods of the classical mechanics it can be shown that if we take b, the distance between the center of the ion and the nuclei, as unity, then the maximum displacement of the electron from the center (i.e., at the end of its path) is 2.214. The velocity of the electron when it passes the center of the ion is such that if it should continue to move with this velocity it would travel a distance 5.148 during the time that it actually takes to move from the center to the point furthest from the center. The total energy W of the ion is $0.6468\ W_0 a_0/b$. As soon as b is known the ionizing potential of hydrogen corresponding to this model can be calculated.

I have tried to apply the quantum theory in two different ways, although without certainty that either way is correct. According to the first method I have assumed that the angular momentum (or the moment of momentum) of the electron about each of the nuclei is $h/2\pi$ when the electron passes through the center. Of course the angular momentum about one of the nuclei decreases as the electron moves further from the center but this is due to the fact that the momentum is imparted to the other nucleus. A consideration of Landé's models for the octet, as well as the model which I previously proposed for the helium atom, suggests that in structures having more than one electron and one nucleus, we are concerned not with the momentum possessed by any electron, but rather with the momentum which is *transferred* from one electron to another or from an electron to a nucleus. On the basis of this assumption, it can be readily calculated that the value of b, the distance of the nuclei from the center, is $0.4250\ a_0$ or 0.225×10^{-8} cm. The energy of the ion is then $1.522\ W_0$. Since this is larger than that for the hydrogen atom, this ion will be stable. The difference between this energy and that for the hydrogen molecule (i.e., $0.748\ W_0$) corresponds to the energy required for ionization. Expressed in volts

[1] See particularly Franck, Knipping and Krüger, *Deut. Phys. Ges. Verh.* **21**, 728 (1919).

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this 10.15 volts, which is in fair agreement with the experimental values (11 to 11.5 volts).

In the second method of applying the quantum theory I have used the relation $\int pdq = h$ where I have taken q to be the distance measured from the center along the rectilinear path, and p is the momentum in the direction of this path. As far as I know there is no good reason for choosing this particular co-ordinate system except that it seems to be the simplest. These assumptions lead to the value $b = 0.5261\ a_0 = 0.279 \times 10^{-8}$ cm. The energy is then $1.229\ W_0$, which again corresponds to a stable hydrogen ion but the ionizing potential is 14.1 volts.

The evidence in favor for these models is far from conclusive but in view of the fact that Bohr's models for the hydrogen molecule and ion can be correct it seems important to test out the new models in as many ways as possible. The mathematical calculations upon which these models are based will probably be published in the *Physical Review*.

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THE DIFFUSION COEFFICIENT IN SOLIDS AND ITS TEMPERATURE COEFFICIENT

With SAUL DUSHMAN as co-author

Physical Review

Vol. XX, No. 1, 113, July (1922).

CONSIDER a solid as consisting of layers of atoms, δ being the distance between layers. Let Kdt be the probability that a given atom in a layer A shall move into the adjacent layer B during the time dt. Then the diffusion coefficient is

$$D = K\delta^2. \tag{1}$$

The quantity K is a frequency analogous to the velocity constant of a unimolecular chemical reaction. The velocity of such reactions is approximately given by the semi-empirical relation

$$K = \nu e^{-h\nu/kT} \quad \text{or} \quad K = \frac{Q}{Nh} e^{-Q/RT}, \tag{2}$$

where ν or Q is characteristic of the reaction. It is now shown that this relation also holds for the K calculated by (1) from the diffusion coefficient. For the diffusion of thorium through tungsten at 2300°K $D = 1.1 \times 10^{-9}$ cm^2 sec^{-1}. Substituting this in (1) and (2) gives $Q_{cal} = 90{,}500$ g calories per g molecule. Plotting log D_{obs} against the reciprocal of the temperature, from 1900 to 2500°K, gives a straight line from whose slope we get $Q_{obs} = 94{,}000 \pm 3000$, in satisfactory agreement with Q_{cal}. Even better agreement is obtained from published data of Roberts-Austin on diffusion of gold in lead and of Warburg and Schulze on diffusion of sodium ions in glass. Thus the temperature coefficient of D may be calculated if the value of D is known at one temperature.

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THE DISTRIBUTION AND ORIENTATION OF MOLECULES

Colloid Symposium Monograph
Vol. III, 48 (1925).

WHEN THERMAL equilibrium prevails the distribution of molecules between two regions in which the potential energies of the molecules are different is given in general by the Boltzmann equation

$$\frac{n_1}{n_2} = e^{\lambda/kt} \tag{1}$$

Here n_1 and n_2 are the numbers of molecules per unit volume in Regions I and II and λ is the potential energy which must be expended to move a molecule from Region I to Region II, while T is the absolute temperature and k is the Boltzmann constant[1] 1.372×10^{-16} erg per degree. This equation is closely related to the well known Nernst equation for the electromotive force of a concentration cell.

Equation (1) cannot usually be directly applied to the distribution of molecules between separate phases. For example, if we consider the equilibrium between a liquid and its vapor and let n_2 be the concentration in the vapor and n_1 that in the liquid phase we find that (1) must be replaced by

$$\frac{n_1}{n_2} = Ae^{\lambda/kt} \tag{2}$$

The factor A corresponds to the integration constant of the Clapeyron equation for vapor pressures, and its theoretical value must be determined in accordance with the third law of thermodynamics.

A generalized form of the Boltzmann equation has been much used in recent years:

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} e^{\lambda/kt} \tag{3}$$

[EDITOR'S NOTE: This paper appears as Chapter Six in the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

[1] The Boltzmann constant is merely the gas constant R expressed per molecule instead of per gram molecule.

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Here p_1 and p_2 are defined as the *a priori probabilities* of the molecules in the two regions or two states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. Fortunately the factors p_1 and p_2 vary little if any with temperature and, in the case of related phenomena, the values of p_1/p_2 are often nearly alike, or at any rate their variations produce an effect which is usually small compared to that caused by the exponential factor. Thus the generalized Boltzmann equation becomes of great practical value even when we do not possess sufficient theoretical knowledge to determine the value of the probability coefficients.

The ratio of the concentration n_1/n_2 is also equal to the ratio P_1/P_2 of the actual probabilities per unit volume for the existence of molecules in the two states, so that

$$\frac{P_1}{P_2} = \frac{p_1}{p_2} e^{\lambda/kt} \tag{4}$$

This equation may be applied for example to study the probability of any particular orientation of a molecule in a liquid, with respect to neighboring molecules or to deal with the orientation of molecules in adsorbed films at interfaces between phases. Equation (3) on the other hand may be used in studying the distribution of molecules between phases and interfaces and also in considering the segregation of certain molecules in the neighborhood of others, due to the local fields of force. Debye and Hückel (*Phys. Zeitschr.* 24, 185, 305 (1923)) for example have recently used the Boltzmann equation to determine the segregation of negative ions around positive ions (and *vice versa*) and have thus evolved a new theory of electrolytic solutions.

Before we can use Equations (3) and (4) in the way suggested, it is necessary to have definite knowledge of the energy change λ involved in the change of state.

In the case of the molecules of organic substances of non-polar type the so-called physical properties are usually roughly additive. For example, the addition of each CH_2 to a hydrocarbon chain in most compounds containing such chains increases the volume, raises the boiling-point, and alters the solubilities in approximately the same way. It is reasonable to assume, therefore, that the field of force about any particular group or radical in a large organic molecule is characteristic of that group and, as a first approximation, is independent of the nature of the rest of the molecule. For convenience we shall refer to this as the *principle of independent surface action.*

It will be readily recognized that this principle lies at the foundation of the theory proposed by the writer in 1916, according to which the surface tension of pure liquids and the properties of adsorbed films at interfaces depend largely upon the orientation of the molecules in the interfaces.

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Thus the surface energy[2] γ of all the normal saturated aliphatic alcohols is the same as that of the saturated hydrocarbon hexane, namely 50 ergs per cm^2. The actual surface energy is that of a hydrocarbon surface in both cases. The alcohol molecules should not be regarded as being packed side by side and arranged with the axes of the hydrocarbon part of the molecule perpendicular to the surface, for there is no force which would compel them to be so arranged. The alcohol molecules which are temporarily in the surface will be free to respond to thermal agitation exactly as if they were in the interior of the liquid, with the single exception that the hydroxyl group cannot itself (for any appreciable fraction of the time) form part of the actual free surface of the liquid. The interaction between the hydroxyl groups of different molecules in the surface is thereby not appreciably altered by the fact that these molecules are forming part of the surface.

The fact of most interest at present is that the hydroxyl group, even in such a small molecule as that of methanol, does not materially alter the surface energy of the CH_3 group which is able to form the actual surface of the liquid by the orientation of the molecule.

The reason that the hydroxyl group avoids the surface must be sought in the energy of the field surrounding this part of the molecule. But by ordinary surface tension and interfacial surface tension measurements we have knowledge of the forces by which hydroxyl groups and hydrocarbon surfaces interact. Let us see whether from such knowledge we cannot determine the energy involved in the orientation of an alcohol molecule and then find from the Boltzmann equation whether this energy is sufficient to cause the orientation indicated by the experiments.

For this purpose let us consider a molecule of methanol. From the density, molecular weight and Avogadro number we find that the volume[3] per molecule is $67.A^3$. Assuming close-packed spheres this gives a molecular surface of $65.A^2$ and a diameter of 4.56A. These figures would not be materially altered if we should assume any other reasonable shape for the molecule. We may take half the surface to consist of the hydroxyl group while the CH_3 radical occupies the other half, these areas being each $32.5A^2$.

Imagine a molecule of methanol half immersed in a liquid consisting of other methanol molecules as illustrated diagrammatically in Fig. 1. We use R to denote a hydrocarbon radical and X to denote an active group such a hy-

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[2] The total surface energy γ is related to the free surface energy γ_f by the equation $\gamma = \gamma_f - -T(d\gamma_f/dT)$. The total energy γ is nearly independent of temperature. From the linear decrease of γ_f with increasing temperature it is probable that the variation of γ_f is a direct result of the thermal agitation of the molecules rather than being due to any change in the structure of the surface. The total energy γ is therefore the quantity which will indicate most clearly any orientation of molecules in the surface.

[3] We shall express the dimensions of molecules in terms of the Ångstrom unit 10^{-8} cm. Areas will be expressed in A^2 (10^{-16} cm^2) and volumes in A^3 (10^{-24} cm^3).

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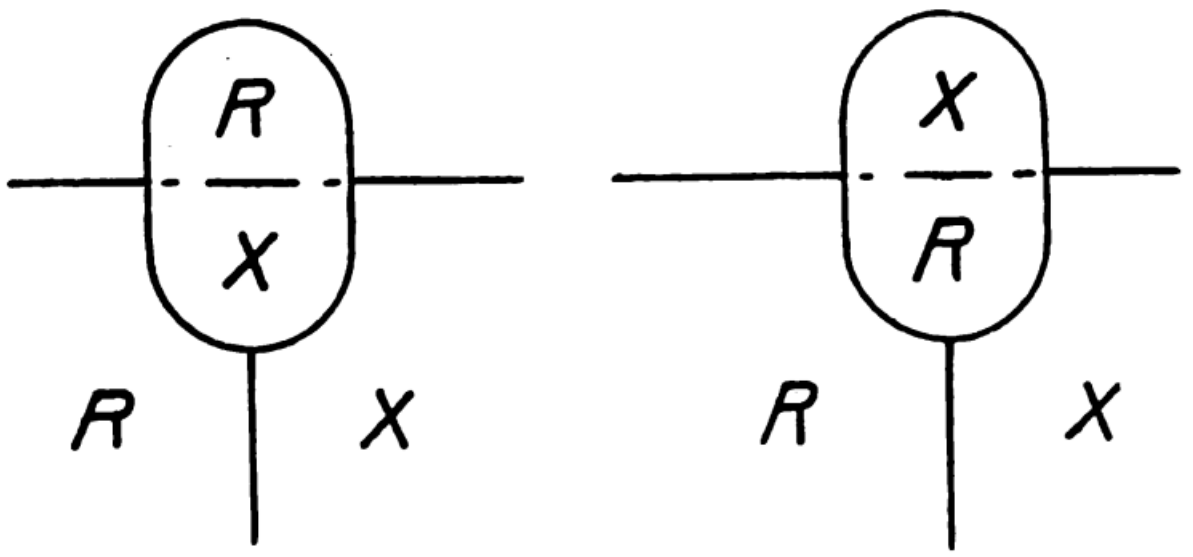
droxyl. Let us for the present disregard the structure of the liquid and the orientation of the neighboring molecules and consider roughly that half the liquid in contact with the given molecule consists of CH_3 while the other half is OH. as suggested in the diagram. Let us now calculate the surface energy corresponding to the two orientations indicated. If S is the surface of the molecule, γ_R the surface energy of CH_3 and γ_{RX} the interfacial energy between CH_3 and OH radicals then the total surface energy of the molecule in Position *a* is $\frac{1}{2}S\gamma_R + \frac{1}{4}S\gamma_{RX}$ while in Position *b* it is $\frac{1}{2}S\gamma_X + S\gamma_{RX}$. Thus the difference in energy between the two positions which is available for causing the orientation is

$$\lambda = \tfrac{1}{2}S(\gamma_X - \gamma_R) \tag{5}$$



Position *a*. Position *b*.

FIG. 1. Two conceivable orientations of a molecule in the surface of Methanol.

Measurements of the surface energy of hydrocarbons give $\gamma_R = 50$ ergs per cm². The surface energy of water at 20° is 117, but since the water molecules are decidedly polar they will undoubtedly be oriented in the surface so that this value represents the energy of the least active part of the molecule. We shall see from data on the heat of evaporation of water and alcohol that a more reasonable value for γ_X is 190 ergs per cm². Placing $S = 65.A^2$ in Equation (5) we find $\lambda = 22\times10^{-14}$ or 46×10^{-14} erg according as we take 117 or 190 as the value of γ_X.

The degree of orientation of the molecules can now be calculated from the Boltzmann equation (4). The probability coefficients p_1 and p_2 may be taken equal since the geometrical probabilities of the two orientations are the same. Putting $T = 293°$ we find $kT = 4.0\times10^{-14}$ erg. Thus the exponent is 5.5 or 11.5 according to the two values of γ^-. The corresponding probability ratios P_2/P_1 are 300 and 100,000 respectively.

Thus with the lower value of γ_X the probability of the orientation *a* in Fig. 1 is 300 times greater than that of *b* while with the higher and more reasonable value of γ_X the ratio is 100,000 to 1.

A more complete justification of the use of the principle of independent

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surface action is being published elsewhere[4]. A brief summary of the principal results will be given here and then further applications will be made, chiefly dealing with adsorbed films at interfaces.

Evaporation of Pure Substances

Consider a molecule AC (Fig. 2) whose surface S is composite and let a represent the fraction of its surface which is of one kind A (say a hydrocarbon chain)

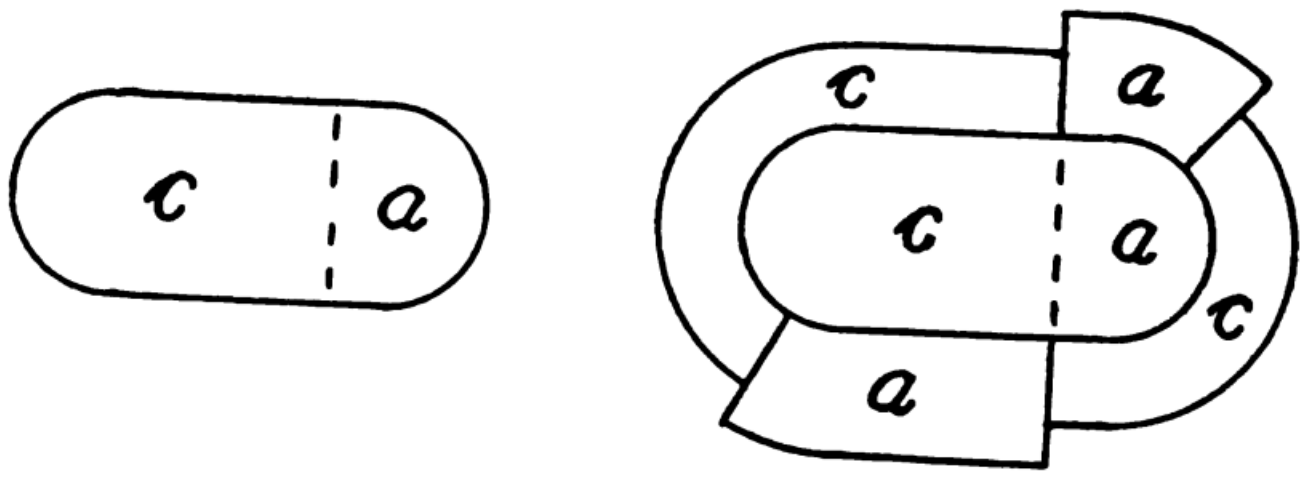

FIG. 2. Diagram of a molecule AC and of the same molecule in liquid AC.

while c is the fraction of the surface which is of the second kind C (say one or more hydroxyl groups). Then

$$a+c=1 \tag{6}$$

If we are dealing with a pure liquid each molecule is surrounded by others of the same kind. As a first approximation let us assume that the molecules around a given molecule are neither orientated nor segregated but are arranged in a purely random manner as if no surface energies, λ, were acting. We shall consider later by means of the Boltzmann principle what errors are made by this simplifying assumption.

In Fig. 2 the molecule AC is shown first by itself and secondly, surrounded by others in such a way that the relative areas of the two kinds of surface in contact with each part of the given molecule are in the ratio of a to c.

The area of that part of the molecule which has an A-surface is Sa and of this the fraction c is in contact with the C-surface of surrounding molecules. The corresponding surface energy is $Sac\gamma_{ac}$. Where the A-surface of one molecule is in contact with the A-surface of another there is of course no surface energy.

Similarly the area of contact of the C-surface of the given molecule with the A-surface of neighboring molecules is Sca and the corresponding energy

[4] A general discussion of the mechanism and the nature of the forces at the surfaces of molecules and applications of the independent surface action to orientation will be published in the book on Colloid Chemistry being edited by Jerome Alexander. A paper giving a detailed mathematical treatment of vapor pressures of liquids and their binary mixtures and of the mutual solubilities of liquids, together with a comparison with available experiment data, is being submitted to the *Journal of Physical Chemistry* for publication.

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is $Sac\gamma_{ac}$. Thus the total surface energy of a given molecule in contact with others is $2Sac\gamma_{ac}$.

Let us now remove the molecule AC to a vapor phase so that it is not in contact with others. Then at the surface of the molecule there is the energy $S(a\gamma_a+c\gamma_c)$ and there is an equal surface energy at the surface of the cavity in the liquid. This latter disappears when the cavity is allowed to collapse but at the same time the new energy $Sac\gamma_{ac}$ appears because of the new interfacial contacts. This energy $Sac\gamma_{ac}$ is half as great as the original energy of the molecule in the liquid, the factor $\frac{1}{2}$ being due to the fact it takes *two* opposing surfaces to make an interface. Thus when the surface S collapses the total interfacial area formed (counting surfaces AA and CC) is only $\frac{1}{2}S$.

The increase in surface energy involved in transferring a molecule from the liquid to the vapor phase is thus

$$\lambda = S(a\gamma_a - ac\gamma_{ac} - c\gamma_c) \tag{7}$$

However if the molecule is a large one it may be so flexible that surface forces tend to make it assume a spherical form when it is in the vapor phase although it may be chain-like in the liquid phase. Also, active groups such as hydroxyl will tend to be drawn into the interior of a large molecule of vapor, just as they are drawn below the surface of the liquid phase. We may neglect the change in S in passing from the liquid to the vapor phase, but may profitably consider that the surfacefrac tions a and c are different in the two cases.

If a_vS and c_vS are the areas of A-surface and C-surface in the molecule of vapor, then $(a\text{-}a_v)$ is the A-surface which becomes buried within the molecule of vapor. Thus we find that the energy for the transfer of a molecule from the liquid to the vapor is

$$\lambda = S[a_v\gamma_a + (a - a_v - ac)\gamma_{ac} + c_v\gamma_c] \tag{8}$$

An analysis of the available data on the heats of evaporation and boiling points of hydrocarbons and alcohols shows that the variation of λ with chemical composition and structure is in excellent agreement with this equation, even in the case of mono-, di- and tribasic alcoho ls and the compounds having branching chains.

The surface energies γ which give best agreement with these data are

$$\begin{aligned} \gamma_R &= 32.7 \text{ for } CH_3 \text{ groups} \\ \gamma_R &= 38.2 \text{ for } CH_2 \quad ,, \\ \gamma_X &= 190 \quad \text{for OH} \quad ,, \\ \gamma_{RX} &= 34 \quad \text{for the interfacial energy of OH against R (hydrocarbon)} \end{aligned} \tag{9}$$

The results show unmistakably the tendency for the larger hydrocarbon molecules of vapor to become spherical and for the hydroxyl group to become partly submerged under hydrocarbon groups in the vapor molecule especially when the hydrocarbon chain is long enough for its end to reach back to the hydroxyl

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group without too sharp curvature. In molecules containing more than one hydroxyl there is a particularly strong tendency for the hydroxyls to come into contact with each other. The surface energies involved in these changes in configuration are sufficient, according to the Boltzmann equation, to overcome the effects of thermal agitation and probably of the constraints due to imperfect flexibility of the molecules.

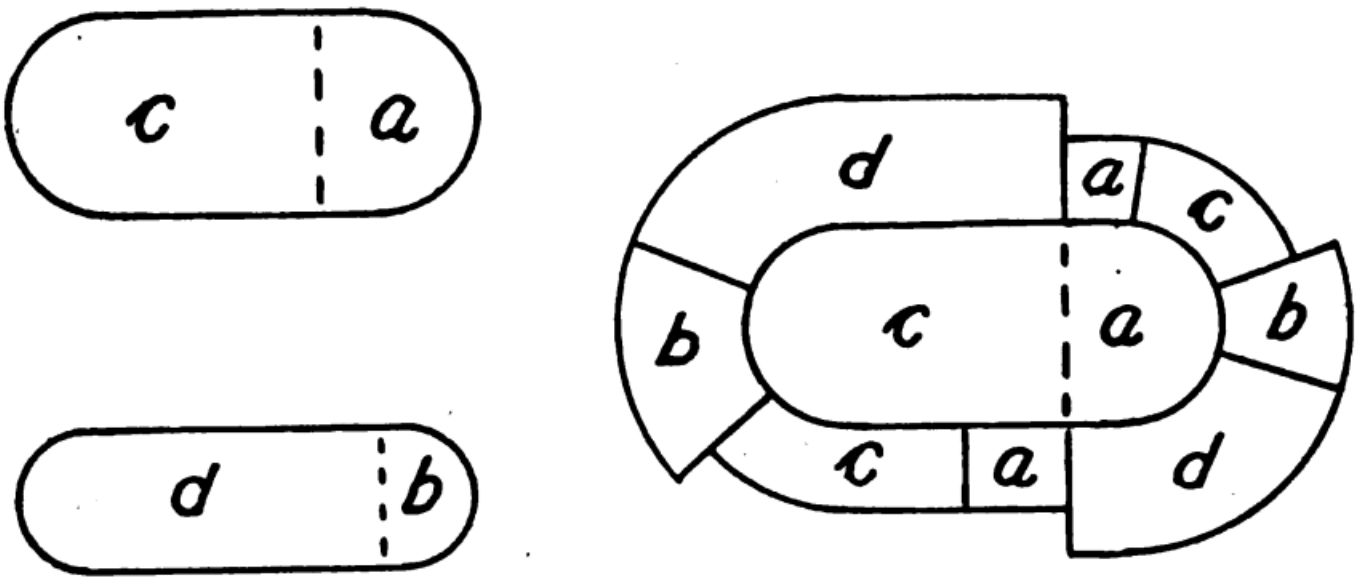

FIG. 3. Diagram of molecules A and B and of a molecule A in a mixture of A and B.

It is believed that more accurate measurements of vapor pressures of a variety of organic compounds can lead to the development of very definite knowledge of the configurations of their molecules in the vapor phase.

Vapor Pressures of Binary Mixtures

Let us now calculate the energy λ needed to transfer one molecule in a binary mixture to another mixture of the same components having different concentrations. Let us designate the two types of molecules corresponding to the two components by A and B as indicated in Fig. 3. Each molecule is assumed to have a composite surface. The fraction a of the surface of the molecule A is an A-surface, while the fraction c is a C-surface. Similarly b and d are the fractions of the surface of the B molecule which are occupied by B- and D-surfaces respectively, so that

$$a+c=1 \text{ and } b+d=1 \tag{10}$$

Let us now consider a binary mixture in which the mol-fraction of A-molecules is A and the mol-fraction of B-molecules is B. The righthand section of Fig. 3 represents an A-molecule in such a binary mixture. We assume as before that there is neither orientation nor segregation of the molecules which surround a given molecule. Then the relative probabilities that any point on one molecule shall be in contact with an A-molecule or with a B-molecule is proportional to the *total surface areas* of the two kinds of molecules in the mixture. It is thus useful to express the concentrations of the two components A and B in terms of their *surface fractions* which may be defined by the equations

$$\alpha=\frac{S_A A}{S_A A+S_B B} \quad \text{and} \quad \beta=\frac{S_B B}{S_A A+S_B B} \tag{11}$$

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where S_A and S_B are the surface areas of the A- and B- molecules respectively. The fractions α and β as well as A and B are related:

$$A+B=1 \quad \text{and} \quad \alpha+\beta=1 \tag{12}$$

The surface energy of the A-molecule in the liquid is now found by adding together the energies of each of the five interfaces: AB, AC, AD, BC, and CD. Consider for example the interface AD. The area of the A surface of the A-molecule is aS_A. Of this surface, the fraction β is in contact with B-molecules and of this area of contact the fraction d is a contact with the D-surface. The corresponding surface energy is thus $S_A a\beta d\gamma_{ad}$. For all five terms the surface energy λ_1 is

$$\lambda_1 = S[2\alpha ac\gamma_{ac}+\beta(ab\gamma_{ab}+ad\gamma_{ad}+bc\gamma_{bc}+cd\gamma_{cd})] \tag{13}$$

Now let us imagine that the A-molecule is removed to a vapor phase, leaving a cavity in the liquid. The surface energy λ_2 of the molecule in the vapor phase is

$$\lambda_2 = S(a\gamma_a+c\gamma_c) \tag{14}$$

and the surface energy of the cavity is

$$\lambda_3 = S_A[\alpha(a\gamma_a+c\gamma_c)+\beta(b\gamma_b+d\gamma_d)]$$

When the cavity is allowed to collapse the surface energy λ_3 disappears and new interfaces having the energy λ_4 are produced. The value of λ_4 is found by the summation of 12 terms. The surface of the cavity, before collapse, consists of the areas: $A_A a^4$, $S_A ab$, $S_A \beta b$ and $S_A \beta d$ of the four kinds of surfaces A, B, C and D. Considering that each of these surfaces forms contact with the others in proportion to their respective areas and remembering that it takes two faces to make an interface, we find that the energy λ_4 is

$$\lambda_4 = S_A[\alpha^2 ac\gamma_{ac}+\beta^2 bd\gamma_{bd}+\alpha\beta(ab\gamma_{ab}+ad\gamma_{ad}+bc\gamma_{bc}+cd\gamma_{cd})] \tag{15}$$

The energy λ that must be expended in transferring an A-molecule from the liquid phase to the vapor is then

$$\lambda_{AV} = \lambda_2+\lambda_4-\lambda_1,$$

the energy λ_3 dropping out. Substituting into this the values from Equations (13), (14) and (15) and replacing α by its value $1-\beta$ we thus find

$$\lambda_{AV} = S_A(a\gamma_a-ac\gamma_{ac}+c\gamma_c-\varphi\beta^2) \tag{16}$$

where φ is independent of the concentrations of the components and is a function of the γ's:

$$\varphi = ab\gamma_{ab}+ad\gamma_{ad}+bc\gamma_{bc}+cd\gamma_{cd}-ac\gamma_{ac}-bd\gamma_{bd} \tag{17}$$

In the case of the evaporation of a pure liquid A we place $\beta = 0$ in (16) and find for the energy of evaporation

$$\lambda' = S_A(a\gamma_a-ac\gamma_{ac}+c\gamma_c) \tag{18}$$

so that Equation (16) simplifies to

$$\lambda_{AV} = \lambda'_{AV}-S_A\varphi\beta^2 \tag{19}$$

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If we have two binary mixtures (1 and 2) having the same components but in different concentrations, the energy required to transfer an A-molecule from 1 to 2 is, according to (19)

$$\lambda_A = S_A\varphi(\beta_2^2-\beta_1^2) \tag{20}$$

and in a similar way it may be shown that the energy of transfer of a B molecule from 1 to 2 is

$$\lambda_B = S_B\varphi(\alpha_2^2-\alpha_1^2) \tag{21}$$

As the first application of these equations let us make a comparison of the energy λ_A' for the transfer of a molecule A from a pure liquid A to a pure liquid B, with the energy λ_B' for the transfer of a B molecule from B to A. In liquid A, $\alpha = 1$ and $\beta = 0$ while in B, $\alpha = 0$ and $\beta = 1$ and Equations (20) and (21) reduce to

$$\lambda_A' = S_A\varphi \quad \text{and} \quad \lambda' = S_B\varphi \tag{22}$$

The energy of transfer of molecules A and B between two pure liquids A and B is thus proportional to the surface areas of these molecules.

The Boltzmann equation may now be used to calculate the distribution of molecules between the vapor phase and a binary mixture of liquids. If we let p_A be the partial pressure of the A-molecules in the vapor then by the generalized Boltzmann equation (3) we have

$$\frac{p_A}{A} = Ke^{-\frac{\lambda_{AV}}{kT}} \tag{23}$$

where λ_{AV} is given by Equation (19) and K is a constant into which are grouped as factors the *a priori* probabilities and the dimensional factors needed to allow us to express the concentrations in the liquid in terms of the mol-fraction A while that of the vapor phase is expressed as a pressure p. We are hereby making the tacit but reasonable assumption that the probability coefficients are independent of the concentrations of the components. The vapor pressure P_A of the pure liquid A is given by (22) if we place $A = 1$ and $\lambda_{AV} = \lambda_{AV}'$ so that

$$P_A = Ke^{-\frac{\lambda_{AV'}}{kT}} \tag{24}$$

Dividing (23) by (24) and by combining with (19)

$$p_A = P_A Ae^{\frac{S_A\varphi}{kT}\beta^2} \tag{25a}$$

and in a similar way the partial pressure of component B is

$$p_B = P_B Be^{\frac{S_B\varphi}{kT}\alpha^2} \tag{25b}$$

These equations for the vapor-pressures of binary mixtures reduce to the well known Raoult's law when $\varphi = 0$, that is, when the energy of mixing is zero.

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Comparison with experimental data, particularly with the accurate data of Zawidski (J. v. Zawidski, *Zeit. phys. Chem.* **35**, 129–203 (1900)) shows that even for liquids which depart considerably from Raoult's law these equations, which involve only one adjustable constant φ, usually agree with the data within the experimental error. In the case of mixtures in which S and S differ considerably, the use of these factors and the use of the surface fractions α and β instead of the mol fractions, are found to be thoroughly justified.

The rather meager experimental data available show that in changing from one member of a homologous series of compounds to another, in a given type of mixture, the values of φ change in general in the manner indicated by (17).

Some typical values of φ calculated from published experimental data on vapor pressures of binary mixtures are given in Table I. It is seen that the values of φ are of the order of magnitude of the surface tensions of liquids, but are smaller than these in accord with the fact that in Equation (17) (which gives φ) the coefficients are all less than unity and two of them are negative.

It can be shown from (17) that φ should approach zero if the A molecules and the B molecules become alike in regard to both their values of γ and their surface fractions a and b. We see from Table I that the observed values of φ are

TABLE I

"Mixture Energies" φ for Various Binary Mixtures

Mixture	Ref.[5]	Temp. °C	φ ergs per cm^2
1. Carbon disulfide-Acetone	Z	35	+ 6.9
2. Water-Pyridine	Z	80	+12.9
3. Carbon tetrachloride-Ethyl acetate	Z	50	+ 1.18
4. Ethyl acetate-Ethyl iodide	Z	50	+ 1.90
5. Ethyl iodide-Carbon tetrachloride	Z	50	+ 0.9
6. Hexane-Ethyl iodide	v. H.	60	+ 2.6
7. Acetone-Chloroform	S	50	− 2.9
8. Carbon disulfide-Chloroform	S	50	+ 2.15
9. Benzene-Chloroform	S	40	− 0.4
10. Benzene-Ethyl ether	S	40	− 0.1
11. Benzene-Toluene	S	40	+ 0.50
12. Benzene-Carbon tetrachloride	Z	50	+ 0.57
13. Benzene-Carbon disulphide	S	40	+ 2.1
14. Benzene-Methyl acetate	S	40	+ 2.5
15. Benzene-Methanol	S	40	+10.1
16. Methanol-Ethanol	S	40	0.0
17. Methyl acetate-Ethyl acetate	S	40	+ 0.4

[5] Data indicated by Z are those of Zawidski (*l.c.*); S are from rough measurements of the total pressures of binary mixtures, by G. C. Schmidt, *Zeit. phys. Chem.* **99**, 71 (1921); v. H. is from H. v. Halban, *Zeit. phys. Chem.* **84**, 129 (1913).

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very small for mixtures of closely related substances such as ethanol-methanol, benzene-toluene, and methyl acetate-ethyl acetate. The series of benzene mixtures 9 to 15, which are arranged in the order of the φ's, show how φ increases as the substance mixed with the benzene becomes less like it, until with methanol φ becomes 10 ergs per cm^2.

In the case of mixture No. 6, hexane-ethyl iodide, there are only two kinds of molecular surface (R and I) and therefore the 6 terms of Equation (17) reduce to one, so that the value of γ (R-I) can be calculated from the observed value of φ. The three binary mixtures Nos. 3, 4 and 5 involve only 3 components. Because of the symmetry of carbon tetrachloride ($a = 1$, $c = 0$) and the fact that ethyl acetate and iodide both contain hydrocarbon (R) surfaces, Equation (17) becomes much simplified. By means of the values of φ for the 3 mixtures Nos. 3, 4 and 5 we obtain 3 equations containing 5 unknown values of γ. From a study of the surface tensions and other properties of alkyl chlorides and iodides we may conclude that chlorine has properties intermediate between alkyl and iodine. Thus it is reasonable to assume that γ(Cl-I) $= \gamma$(R-Cl). We have seen in (9) that γ(R-OH) = 34 and there are several indications that the relation of -COO- to R is not materially different from that of OH to R. Thus we place γ(R-C) = 34, using C as an abbreviation of the -COO- group in esters. We then have five equations for our five unknowns and thus find the values given in Table II.

TABLE II

Values of Surface Energy γ Calculated from Experimental Data on Vapor Pressures

Surfaces	Symbol	γ ergs per cm^2
1. Hydrocarbon-Iodine	γ(R-I)	13.7
2. Hydrocarbon-Chlorine	γ(R-Cl)	4.1
3. Hydrocarbon-COO-	γ(R-C)	33.7
4. Chlorine-Iodine	γ(Cl-I)	4.1
5. Chlorine-COO-	γ(Cl-C)	17.7
6. Iodine-COO-	γ(I-C)	16.6

From these values it should be possible to calculate the vapor pressures of any binary mixtures of compounds such as RCl, RI, RCOOR where each R represents any alkyl group. There is also no difficulty in including compounds containing two or Cl, I or -COO- groups.

It should also be possible from the principles that have been outlined to develop equations for ternary mixtures and for those containing compounds with molecules having three or more kinds of surface. Thus from the values of γ in Table II we should be able to calculate the partial vapor pressures of

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a ternary mixture consisting of say propyldi-chlor acetate, ethylene chloride and amyl iodide, from the vapor pressures of the separate components and the ordinary data of molecular volumes.

Unfortunately there have been very few experimental studies of the vapor pressures of a series of related compounds which can serve at present as a test of this theory.

Measurements are needed of the vapor pressures of binary mixtures of hexane with different simple alkyl compounds such as ethanol, propionic acid, ethyl chloride, etc. From each such mixture studied, a separate value of γ can be obtained and it would then be easy to calculate the vapor pressures of other mixtures of such compounds, and thus check the theory by corresponding experiments.

The boiling points of many binary mixtures of alcohols, bromides, iodides and acetates have been measured by Holley (*J. Amer. Chem. Soc.* **24**, 448 (1902)) and by Holley and Weaver (*J. Amer. Chem. Soc.* **27**, 1049 (1905)). For mixtures containing 0.5 mol fraction of each component the total vapor pressure of the mixture was compared with that of the separate pure components and then by a series of trials the partial pressure and φ were calculated by Equations (25).

TABLE III

Observed and Calculated Mixture Energies φ for Binary Mixtures of Alkyl Bromides and Alcohols

Alcohol	Propyl bromide		Iso (?)-Butyl-bromide		Amyl bromide	
	φ_{obs}	φ_{cal}	φ_{obs}	φ_{cal}	φ_{obs}	φ_{cal}
Methanol	8.90	8.76	7.33	8.52	7.30	8.33
Ethanol	6.97	5.82	6.61	5.58	5.90	5.40
Propanol	5.39	4.52	3.24	4.28	—	—
Butanol	3.43	3.76	2.89	3.53	—	—
Pentanol	3.77	3.21	—	—	—	—

Table III gives a summary of the values φ_{obs} which were thus obtained from the experimental data on mixtures of bromides with alcohols. The values marked φ_{cal} have been calculated [6] by Eq. (17) from the following values of γ.

Hydrocarbon-bromine $\gamma(\text{R-Br}) = 10.$ ergs per cm^2.
Hydrocarbon-hydroxyl $\gamma(\text{R-OH}) = 33.7$
Bromine-hydroxyl $\gamma(\text{Br-OH}) = 49.6$

[6] The surfaces S of the molecules were calculated from the molecular weights and the densities at room temperature, assuming arbitrarily close packed spheres. The surface fractions a, b, c and d were calculated by taking for the surface of the bromine atom 25.A^2 and for the hydroxyl group 30.A^2.

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The value of γ(R-Br) was assumed to be 10 as a reasonable interpolation between γ(R-I) = 13.7 and γ(R-Cl) = 4.1 as given in Table II. The values of γ(R-OH) and γ(Br-OH) were then determined by least squares to make the agreement as good as possible between φ_{obs} and φ_{cal} in Table III.

Considering the rather rough nature of these data and the uncertainty in some cases as to whether the normal or iso-compounds were used, the agreement is as good as could be expected. The signs of the differences between φ_{obs} and φ_{cal} seem to be distributed nearly at random.

It is interesting to note that the value of γ(R-OH) = 33.7 obtained from these data on the vapor pressures of mixtures of bromides and alcohols agrees with the value 34 given in (9) for γ^{RX} which corresponds to the energy of the same kind of interface, but determined in an entirely different way, viz., from the heats of evaporation of alcohols.

Perhaps the best test of Equation (17) available at present is that based on the published data on the vapor pressures of mixtures of alcohols and water and mixtures of fatty acids and water, although the polar character of these substances undoubtedly causes some mutual orientation and segregation of molecules in these mixtures, so that the assumptions underlying this equation are not completely fulfilled.

Table IV contains the results of calculations based on Wrewsky's data (M. Wrewsky, *Zeit. phys. Chem.* **81**, 1 (1913) and **82**, 551 (1914)) on the partial vapor pressures of aqueous mixtures of methyl, ethyl and propyl alcohols at temperatures of 30° and 50°.

TABLE IV

The Mixture Energies φ *of Alcohol-Water Mixtures*

Alcohol	a	φ_{obs}	φ_{cal}
Methanol	0.460	6.1	6.02
Ethanol	0.359	11.5	11.69
Propanol	0.305	15.1	15.0

φ_{cal} is based upon
γ(R-OH) = 33.7
γ(R-H_2O) = 37.4 and
γ(OH-H_2O) = −12.6

The value of γ(R-OH) was taken to be the same as found from the data of Table III, and the other two γ'*s* were chosen to make φ_{obs} and φ_{cal} agree as well as possible. The fact that the *two* constants could be chosen so as to give such good agreement with the *three* values of φ_{obs} is evidence for the applicability of Equation (17) from which φ_{cal} was derived.

In these calculations the water molecule was assumed to have a single kind of surface. The value γ = 37.4 is in reasonable agreement with the value

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59 obtained by Harkins for the total surface energy of a hexane-water interface by direct measurement.

TABLE V

The Mixture Energies φ of Fatty Acid-Water Mixtures

Acid	a	φ_{obs}	φ_{cal}
Formic	0.739	−15.0	−13.6
Acetic	0.549	+ 2.5	+ 1.1
Propionic	0.459	+ 8.0	+ 8.5
Butyric	0.402	+13.8	+13.4

φ_{cal} is based upon

γ(R-COOH) = 20.0
γ(R-H_2O) = 51.4
γ(H_2O-COOH) = −31.2

The *negative* surface energy $\gamma = -12.6$ for the interface between water and the hydroxyl group is not contrary to known facts and is an expression of the very strong effect of this radical in increasing the solubility of organic substances in water.

Table V gives a summary of calculations based upon Konowalow's data (*Ann Phys.* **14**, 34 (1881)) on the total vapor pressures of mixtures of water with various fatty acids. The values of γ found from these data are in reasonable agreement with others of similar nature already found. These data are, however, probably only rough. The known existence of double molecules in the vapors of the lower fatty acids should cause deviations from our theory, but the effect is probably not sufficient to prevent the theory from serving as a useful approximation over a wide range of concentrations.

Mutual Solubilities of Liquids

When two immiscible liquids, A and B, are in equilibrium, each has dissolved some of the other, and the partial vapor pressure p_A from one liquid must be the same as the p_A from the other. Thus, from Equations (25) we obtain the following two equations which express the solubilities of the liquids in one another

$$\frac{A_1}{A_2} = e^{\frac{S_{A\varphi}}{kT}(\beta_2^2-\beta_1^2)}$$

and (26)

$$\frac{B_1}{B_2} = e^{\frac{S_{B\varphi}}{kT}(\alpha_2^2-\alpha_1^2)}$$

The subscripts 1 and 2 refer to the two phases.

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If each liquid is only very slightly soluble in the other, the equations take the simple form

$$A_2 = e^{-\frac{S_{A\varphi}}{kT}} \quad \text{and} \quad B_1 = e^{-\frac{S_{B\varphi}}{uT}} \tag{27}$$

If $S_A = S_B$ then $\alpha = A$ and $\beta = B$ and the two Equations (26) can readily be combined to one of the convenient form

$$\frac{1+\Delta}{1-\Delta} = e^{\frac{S\varphi}{kT}} \tag{28}$$

where $\Delta = A_1 - A_2 = B_2 - B_1$.

We then find that $\Delta = 0$ or $A_1 = A_2$ at a critical temperature T_c given by

$$T_c = \frac{S\varphi}{2K} \tag{29}$$

Above this temperature the liquids are miscible in all proportions, so that there is only one phase, while at lower temperatures two phases exist.

The values of φ calculated from these equations come out usually somewhat lower (10 to 30%) than those from vapor pressures and are probably less accurate. Undoubtedly, in mutually saturated liquids, especially near the critical temperature, the conditions are favorable for orientation and segregation of the molecules in the liquids, so that we should not expect our equations for solubilities to hold as well as those for the vapor pressures of mixtures of liquids which mix in all proportions.

Nevertheless, the general agreement between the theory and the experimental data seem very satisfactory, especially if we are willing to consider mainly relative rather than the absolute values of φ.

The effects of the relative surface areas of the molecules indicated by Equations (27) seem to be well verified by the experimental data. Thus, in general, for two substances only slightly soluble in one another, the substance having the molecules of the larger surface shows the lower solubility in the other.

Even when solubilities are large, nearly to the point of complete mixing, the same rule applies. For example, the critical temperature of butyric acid-water mixtures is $-2.5°C$. At $-6°C$ there are two phases. The water phase contains 0.053 mol fraction of butyric acid, but the acid phase contains 0.76 mol fractions of water. The much greater solubility of the water as compared to the acid corresponds to the smaller surface area of the water ($S_B = 37.8A^2$) as compared to that of the acid ($S = 115A^2$). In fact the difference in solubility is almost exactly what the theory indicates, for the value of φ calculated by Equations (26) from A_1/A_2, involving the solubility of the acid, is 16.9 ergs per cm^2 while B_1/B_2, from the solubility of the water, gives very nearly the same value, viz. $\varphi = 9.7$. These are to be compared with $\varphi = 13.6$ from

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Table V for butyric acid-water mixtures at higher temperature from vapor pressure data.

From the very rough data available on the solubilities of higher fatty acids we obtain the values given in Table VI.

TABLE VI

Solubilities of Fatty Acids in Water

n	Acid	Temp.	Observed solubility mol fraction	a	φ_{obs}	φ_{cal}
4	Butyric	−2°	0.052	0.402	10.5	13.3
5	Valeric	16°	0.0062	0.357	15.0	17.3
9	Nonylic	25°	1.4×10^{-5}	0.272	26.0	25.0
14	Myristic	20°	ca. 10^{-8}	0.198	33.0	31.9

The 5th column gives the surface fraction a corresponding to the carboxyl group whose actual surface is taken to be $45A^2$. The 6th column gives the value of φ_{obs} obtained by Equations (26) from the observed value of the solubility while the 7th column gives φ_{cal} which is calculated by Equation (17) with the same values for the γ's as those already used for the calculations of Table V.

It will be seen that the agreement is reasonable and indicates that the marked decrease in solubility of the fatty acids in water as we pass to the higher fatty acids is fully explained by our theory of independent surface action.

It is important to note that the solubility *of water* in the fatty acids does not continue to decrease without limit as the length of chain increases. As soon as the solubilities have become small Equations (27) are applicable. As the length of chain increases a approaches zero and φ approaches the limiting value 51.4 corresponding to $\gamma(\text{R-H}_2\text{O})$ (see Table V). We see, however, from (27) that S_A, the area of the molecule of acid, continues to increase as the chain lengthens and thus A, the solubility of the acid in water, decreases without limit. On the other hand, S, the area of the water molecule, remains constant so that the solubility B, of water in the acid, decreases only because of the increasing φ and thus approaches a limiting value as the chain lengthens.

Orientation of Molecules in a Liquid Phase

Thus far we have considered particularly the distribution of molecules between different phases on the assumption that there is no mutual orientation of the molecules within the phases. Although the agreement of our theory with experiment proves that in the case of many liquids this orienting effect is negligible, it is believed that such orientation (and corresponding segregation) is the main cause of deviations which occur with the more polar substances.

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For example, the vapor pressures of mixtures of alcohols with water give values of φ which are nearly constant or independent of the concentration, except that the values obtained from the partial pressures of water over the mixtures containing more than about 0.5 mol fraction of water give values of φ which are much too low. Thus, although the partial vapor pressures of methanol over the whole range agree with the value $\varphi = 6.1$, and the partial pressures of water from solutions containing less than 0.5 mol fraction of water also agree with this value reasonably well, the values of φ for the higher concentrations of water decrease rapidly, so that with a mixture containing 0.8 mol fraction of water $\varphi = -20$. With ethanol and propanol similar effects exist but are much less marked.

In order to form a more concrete conception of the principles which govern the orientation of organic molecules within a liquid, let us consider the following model. The inner circle in Fig. 4 represents a molecule AC, the sector a being the A-surface. The annular space between the two circles represents diagrammatically the surfaces of the molecules which surround the given molecule AC. In choosing the symbols a, b, c, d to represent the surface fractions we may, without loss of generality, so assign them among the 4 kinds of surface that $b < a < c < d$. When the molecule AC is oriented as shown, with the whole of the B-surface in contact with A-surface, all of the C-surface will be in contact with D-surface and the surface fraction of A-surface in contact with D is $a-b$. Thus the total surface energy is

$$\lambda_1 = S[b\gamma_{ab}+(a-b)\gamma_{ad}+c\gamma_{cd}] \tag{30}$$

Let the molecule AC now be turned so that the A-surface does not come into contact with B but only touches D. Then the total surface energy is

$$\lambda_2 = S[a\gamma_{ad}+b\gamma_{bc}+(c-b)\gamma_{cd}] \tag{31}$$

These two orientations correspond to the extreme values of the surface energy; when A and B are partly in contact with each other the energy λ has intermediate values. The difference $\lambda_2-\lambda_1$ which we shall refer to as λ_0 is thus the greatest surface energy which can be effective in causing orientation.

$$\lambda_0 = Sb(\gamma_{ad}+\gamma_{bc}-\gamma_{ab}-\gamma_{cd}) \tag{32}$$

For convenience let us place

$$\gamma_0 = \gamma_{ad}+\gamma_{bc}-\gamma_{ab}-\gamma_{cd} \tag{33}$$

so that

$$\lambda_0 = Sb\gamma_0 \tag{34}$$

The unique occurrence of b in these expressions is due to the fact that b is the smallest of the surface fractions a, b, c and d because of the convention of nomenclature that we have adopted.

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We may represent any given orientation of a molecule AC in Fig. 4 by a given position of the vector OA with respect to the vector OB. If AC passes through all possible orientations we may imagine OA as passing over all points on a spherical surface. We may represent all orientations within any given solid angle by the ratio of the spherical surface described by the vector OA, to the total spherical surface, this ratio being called a surface fraction.

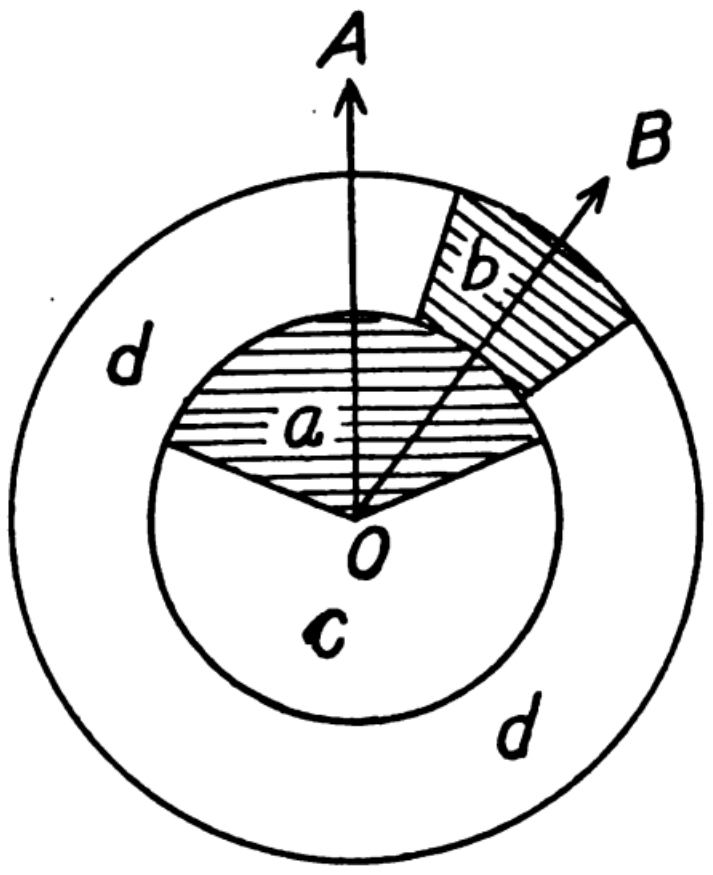

FIG. 4. Diagram illustrating the orientation of a molecule AC in a liquid BD.

The difficulties in the complete solution of the 3-dimensional problem of orientation are considerable and we may therefore content ourselves with treating it as if it were a 2-dimensional problem. We shall assume therefore that the molecule AC in Fig. 4 has cylindrical symmetry and can rotate only about its axis.

There are three cases to consider.

I. The molecule is so oriented that the whole of the B-surface is in contact with A. Surface fraction $(a-b)$.

II. The whole of the B-surface is in contact with C. Surface fraction $(c-b)$.

III. Part of B is in contact with A while the remainder is in contact with B. Surface fraction $2b$.

We may let P be the probability per unit surface fraction that the molecule may be oriented as in Case I. The total probability that a molecule shal be so oriented is thus $P(a-b)$.

The probability that the molecule shall be oriented in Case II may be found by the Boltzmann Equation (4) and is

$$P(c-b)e^{\sigma}$$

where

$$\sigma = \frac{\lambda_0}{kT} = \frac{Sb\gamma_0}{kT} \tag{35}$$

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Within the region corresponding to Case III the surface energy varies linearly between two limits, so that we find the total probability that the molecule shall come under Case III is

$$P\int_0^{2b} e^{\frac{\sigma x}{2b}}\,dx$$

Now since the molecule must be oriented in one of these 3 ways the sum of these 3 probabilities is unity

$$1 = P[(a-b)+(c-b)e^{\sigma}+\int_0^{2b} e^{\frac{\sigma x}{2b}}\,dx \tag{36}$$

If we assume that λ_0 is small enough, σ will be small compared to unity so that we may expand e^{σ} into a series taking only the terms involving the first order in σ. The foregoing equation thus becomes

$$1 = P(1+c\sigma) \tag{37}$$

which gives us the value of P.

We may now determine the average surface energy obtained from all possible orientations by weighting each orientation in proportion to its probability. We thus find, taking only terms up to the first order in σ

$$\lambda = \lambda_1+P\lambda[c+\sigma(c-\tfrac{1}{3}b)] \tag{38}$$

Since $b < a < c$ we may neglect $\frac{1}{3}b$ in comparison with c. Substituting the value of P from (37) we can reduce Equation (38) to

$$\lambda = \lambda_1+\lambda_0 c(1+\sigma a) \tag{39}$$

and by (34) we obtain

$$\lambda = \lambda_1+Sbc(1+\sigma a)\gamma_0 \tag{40}$$

This equation allows us to determine theoretically whether the molecules in a given mixture are oriented to an appreciable extent, and if so, we may then estimate the magnitude of the effect produced. Let us consider the following cases:—

1. $\sigma = -\infty$. Equation (40) is inapplicable, but by the method used in the derivation of Equation (36) we see that all the molecules will be oriented as in Case I and the surface energy is thus equal to λ_1 as given in Equation (30). Practically speaking we have this case, if σ is negative and $-\sigma$ is large compared to unity, which occurs if $-Sb\gamma_0$ is large compared to kT.

2. $\sigma = +\infty$. This case is approached if γ_0 is positive and $Sb\gamma_0$ is large compared to kT. The molecules are nearly all oriented as in Case II so that the energy is λ_2 as given by (31) or

$$\lambda_2 = \lambda_1+\lambda_0 \tag{41}$$

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3. $\sigma = 0$. This corresponds to an entire absence of orienting force. The molecules are thus arranged wholly at random. Equation (40) gives

$$\lambda_R = \lambda_1 + Sbc\gamma_0 \tag{42}$$

Substituting in this the value of λ_1, by (30) and the value of γ_0 from (33) we find

$$\lambda_R = S(ab\gamma_{cb} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd}) \tag{43}$$

Equation (13) was derived as an expression for the energy of a molecule AC surrounded by molecules AC and BD without orientation or segregation. For the case in hand, where AC is surrounded only by molecules BD, we place $\alpha = 0$, $\beta = 1$ and find that Equation (13) then reduces to Equation (43) as of course it should.

4. *σ small compared to unity.* This is the case when $Sb\gamma_0$ is small compared to kT. Equation (40) then applies. Let us consider how the energy λ then differs from λ_R the energy corresponding to random orientation. From (40) and (42) we get

$$\lambda - \lambda_R = Sabc\sigma\gamma_0 = \frac{S^2ab^2c\gamma_0^2}{kT} \tag{44}$$

This equation enables us to estimate what error we have made in the early part of this paper by assuming a random distribution of molecules in liquids, as for example, in the derivation of Equations (11) to (17).

As a specific example, let us apply Equation (44) to calculate the effect of orientation of ethanol molecules in various mixtures of ethanol with hexane. We have already found that the interfacial energy γ(R-OH) is 34 ergs per cm^2. The surface S_A of ethanol molecules may be taken to be 83.5A^2 while that of hexane molecules is 136A^2. The surface $S_A a$ of the hydroxyl group in the ethanol molecule is 30A^2. With these data we find from Equation (17) $\varphi = 4.39$ ergs per cm for ethanol-hexane mixtures and from this, by Equations (25) we can calculate the partial vapor pressures of these mixtures. We now wish to determine what corrections should be applied to these results to take into account the orienting effect of the ethanol molecules on each other.

We see from Equation (20) that the energy needed to transfer an ethanol molecule from pure ethanol to a mixture is

$$\lambda_0 = S_A\varphi\beta^2$$

where β is the surface fraction of hexane in the mixture. This expression was substituted in the exponent of the Boltzmann equation to obtain Equation (25a) which would give the uncorrected vapor pressure of ethanol. To get the corrected vapor pressures we should add to γ_A, before making this substitution, the correction given by Equation (44). We place in Equation (33)

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$\gamma_{ad} = \gamma_{bc} = 34$ and $\gamma_{ab} = \gamma_{cd} = 0$ and obtain $\gamma_0 = 68$. From the value of S_A and S_B we find $a = 0.359$ and $c = 0.641$. Thus Equation (44) becomes

$$\lambda - \lambda_R = 2.72 \times 10^{-14} b^2 \text{ erg} \tag{45}$$

The choice of the value of b is a matter which requires careful analysis. Suppose the mixture is nearly pure hexane containing only a small amount of ethanol. Most of the ethanol molecules will be surrounded only by hexane molecules so that for these molecules $b = 0$. There will be some ethanol molecules, however, whose surface will be in contact with hydroxyl groups of adjacent molecules. For these the value of b will be determined by the area of contact between two hydroxyl groups.

When molecules are arranged like close packed spheres each is in contact with 12 others, so that the area of contact is $S/12$. We may suppose that about 3 of these 12 regions of contact, for the hydroxyl radical in an alcohol, are occupied by the union with the alkyl group. Thus the surface of 30 A^2, which we have taken as the effective surface of the hydroxyl, represents 9 possible regions of contact, each contact having an area of 3.3 A^2. Allowing for a probable deformation we may thus take the area of contact between adjacent hydroxyl groups to be roughly 3.5 A^2, or 4.2 per cent of the whole surface of an ethanol molecule. Since the surface fraction of the hydroxyl in *pure* ethanol is 0.359 and the surface fraction of each contact is 0.042, we see that there should be on the average $0.359/0.042 = 8.5$ hydroxyl groups in contact with each ethanol molecule. In a mixture of ethanol with hexane in which the mol fraction of ethanol is $A = 0.117$ (i.e. 1/8.5) each ethanol molecule will be in contact, on the average, with one hydroxyl group. For such a mixture we may therefore put $b = 0.042$. Equation (45) then gives

$$\lambda - \lambda_R = 0.0048 \times 10^{-14} \text{ erg} \tag{46}$$

With lower concentrations of ethanol the fraction of the ethanol molecules which are in contact with hydroxyl groups is proportional to the concentration. Thus for these low concentrations we obtain for the average energy correction

$$\lambda - \lambda_R = 0.041 \times 10^{-14} A \text{ erg} \tag{47}$$

which gives the same value as (46) when $A = 0.117$.

For higher concentrations of ethanol than $A = 0.117$ there will usually be more than one contact with hydroxyl. However, these will not in general be adjacent but will be distributed nearly according to the laws of chance. If they were distributed absolutely *uniformly* over the surface of the ethanol molecules there would be no tendency to orient these molecules.

According to the probability laws therefore the effective surface area, $S_A b$, of contact with the hydroxyl groups should be proportional to the square root of the number of contacts. Since, by (45) the energy varies as b^2 it is thus directly proportional to the number of contacts or is proportional to the

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concentration A. Therefore Equation (47) gives the value of $\lambda - \lambda_R$ for concentrations above $A = 0.117$, as well as for concentrations below this value.

In general we may thus assume that $\lambda - \lambda_R$ is proportional to A as in Equation (47) and may place

$$\lambda - \lambda_R = MA \tag{48}$$

where M is the proportionality factor.

Going back to the derivation of Equations (25) from (19), (22) and (23) we may now correct the value of λ_{AV} in (19) by means of (48) obtaining

$$\lambda_{AV} = \lambda'_{AV} - S_A \varphi \beta^2 + MA \tag{49}$$

Instead of (24) we then find

$$P_A = Ke^{-\frac{\lambda'_{AV}+M}{kT}} \tag{50}$$

and (25) is replaced by

$$p_A = P_A A e^{\frac{S_A \varphi \beta^2 + MB}{kT}} \tag{51}$$

In the example we are considering (ethanol-hexane) the term MB is $0.041 \times 10^{-14} B$ while $S_A \varphi \beta^2$ is $3.66 \times 10^{-14} \beta^2$ so the effect of orientation of molecules is practically negligible.

In the foregoing analysis we have considered the orientation of a given ethanol molecule by surrounding molecules which are oriented in random directions. Actually these molecules will tend to be oriented by the given molecule and this in turn would increase the orienting effect on the original molecule. It is probable that value of $\lambda - \lambda_R$ given by (45) or (48) should be approximately doubled to take into account this mutual orientation.

In any case we may conclude that with mixtures of many common organic compounds there will be no appreciable orienting effect and that we are therefore justified in assuming a random orientation as a first approximation. The magnitude of the orienting effect is sufficient, however, for it to become of considerable importance as a cause of deviations in the case of polar substances, and particularly of those whose molecules act as dipoles.

Orientation of Molecules in Interfaces

The example of the orientation of alcohol molecules in a free surface which was considered in the introduction has served to show how the principle of independent surface action may be applied in such cases.

When a sufficiently small amount of a substance such as palmitic acid is placed upon a clean surface of water in a tray the surface tension of the water is not appreciably lowered. But if the free surface of the water is decreased, by sliding a strip of paper over its surface, the surface tension begins

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to decrease quite suddenly when the free surface becomes about 20 A^2 per molecule of palmitic acid. By raising the temperature of the water or by introducing traces of acid into the water, the point at which the surface tension begins to decrease may occur at an area of 30 to 50 A^2. Such films may be called expanded films.

In 1917 in a discussion[7] of the arrangement of molecules in adsorbed films on the surfaces of fatty acid solutions it was concluded that in dilute solutions "the hydrocarbon chain lies spread out flat on the surface of the water, but as the concentration of the solution increases, the molecules become more closely packed and when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically." The transition between the two states was assumed to take place in the manner that was suggested *J. Am. Chem. Soc.* **39**, 1865 (1917) for the expanded film of oleic acid, viz., in the expanded film "the molecules are partly reclining on the surface, while in the second case (compressed film) they are packed tightly side by side and are more or less erect upon the surface."

The area covered by a vertically placed palmitic acid molecule is about 20 A^2 while the same molecule lying flat on the surface should cover an area of about 108 A^2. Clearly then the expanded films occupying an area of at most 50 A^2 must consist of molecules which are only slightly inclined from the vertical. As a matter of fact there is no reason at all why the flexible hydrocarbon chains should orient themselves at any particular angle. They will be quite free to respond to thermal agitation and arrange themselves nearly in the same random manner as in a liquid hydrocarbon, the only restriction upon their motion being imposed by the condition that the *lower end* of each molecule must remain in contact with the underlying water. We can thus readily see why the expanded films are *always liquid* while the contracted or fully compressed films of vertically oriented molecules are frequently *solid*. Taking the volume of the hydrocarbon chain in the palmitic acid molecule as 450 A^3 we see that the thickness of the hydrocarbon layer (in A units) will be $450 \div a$ where a is the area of the film per molecule (in A^2 units). Thus when $a = 20$ A^2 the thickness is 22.5 A while for an expanded film for which $a = 33$ A^2 the thickness is 13.6 A.

Consider an expanded film as covering a definite area of a water surface. If additional palmitic acid molecules are introduced into the film there is no change in the area of the free hydrocarbon surface. The energy of transfer of a molecule from any given location to an expanded film is thus the same as the energy of transfer of the molecule to an interface between hydrocarbon and water. The total surface energy λ for a molecule of palmitic acid at the edge of a condensed film is -17 while for a molecule in an expanded film λ is -37. This would indicate that the expanded film should form in pref-

[7] Langmuir, *J. Am. Chem. Soc.* **39**, 1888 (1917).

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erence to the condensed film. However the difference of 20 in the values of λ is not greater than the probable error so that the sign of the difference is somewhat uncertain. In considering the stability of expanded films we must take into account the applied compressive force and the effect of the forces acting between the heads of the molecules which are located in the interface between the hydrocarbon film and the water. To understand these relationships better let us analyze the problem as follows.

Let n molecules of a substance (which spreads on water) be present per unit area as an expanded film on the surface of the water. The flexible hydrocarbon tails of the molecules are subject to little or no constraint except that due to the fact that they are attached to the heads which must remain in contact with the water.

The expanded film may thus be looked upon as a layer of hydrocarbon liquid having at its upper surface a surface energy γ and having adsorbed in its interface with the water n active groups, or heads per unit area. Consider now that by means of a *two-dimensional piston* (for example a paper strip on the surface) the expanded film is allowed to cover only a part of the surface of the water. The spreading force F (in dynes per cm) exerted by the film is measured by the mechanical force applied to the piston. On one side of the piston is a surface of water which exerts a force γ_W tending to cause the film to expand and on the other side is the expanded film whose *upper surface* exerts a force γ_R while the *lower surface* exerts a force which we may represent by γ_L. Thus for equilibrium we have

$$\gamma_W - F = \gamma_R + \gamma_L \tag{51}$$

If the molecules in the film did not have any active groups, the surface tension γ_L would be equal to the normal interfacial energy γ_{RW}. But the *active groups in the interface* because of their thermal agitation will tend to act like a two-dimensional gas. When these active groups or heads are far enough apart they will exert a force F_L following the gas law

$$F_L = nkT \quad \text{or} \quad F_L a = kT \tag{52}$$

where a is the area per molecule.

When the molecules are packed as closely as in the ordinary expanded film, we should, by the analogy with the b term in the van der Waals equation, write

$$F_L(a - a_0) = kT \tag{53}$$

where a_0 is the area per molecule for a highly compressed film.

Furthermore the analogy with the equation of state for gases would suggest that when the film is compressed sufficiently, attractive forces between the active groups would come into play and that these might be largely responsible for the small spreading forces observed with some contracted films. In any case, however, we may place

$$\gamma_L = \gamma_{RW} - F_L \tag{54}$$

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and thus from Equation (51) we get

$$F = \gamma_W - \gamma_R - \gamma_{RW} + F_L \tag{55}$$

For very low compressive forces we may neglect the attractive forces between the heads and thus by combining Equations (55) and (53) we get

$$(F - F_0)(a - a_0) = kT \tag{56}$$

as our equation of state for expanded films. Here F_0 is used as an abbreviation for the three γ terms in (55) so that

$$F_0 = \gamma_W - \gamma_R - \gamma_{RW} \tag{57}$$

Thus we see that we should not expect the simple gas law of Equation (52) to hold for expanded films, but such a law should hold only after constants F_0 and a_0 have been subtracted from the observed values of F and a.

Examination of the experimental data on expanded films in my 1917 paper, and in Adam's papers[8] show that the agreement with Equation (56) is very satisfactory. For large compressive forces deviations occur which are of the kind that are to be expected as a result of attractive forces between the heads of the molecules. For example, Adam's curve (in this 3rd paper) for a film of myristic acid on water at 32.5°C gives the equation

$$(F + 13)(a - 18) = kT$$

The value of a_0 is thus 18.A² while F_0 has the value —13 dynes per cm.

Let us compare this value of F_0 with that calculated by Equation (57). For water at 32.5° the free energy (surface tension) γ_W is 71.0 dynes per cm. The interfacial free surface energy γ_{RW} of octane is 50.4. Since the temperature coefficient is very low the total interfacial energy is about the same as the free energy. Our theory of the structure of the interface leads to the conclusion that the *total energy* is independent of the length of the hydrocarbon chain and since in this case the free energy and total energies are nearly the same the free energy will also be independent of the chain length. Thus for tetradecane (the hydrocarbon corresponding to myristic acid) we may put $\gamma_{RW} = 50.4$.

The free surface energy of octane at 32.5° is 20.4 and the total energy is 48.4. For tetradecane the theory indicates that the total energy will also be 48.4. The free surface energy is a linear function of temperature and becomes zero at the critical temperature. Taking the critical temperature of tetradecane as 680°K we can thus estimate that the free surface energy at 32.5°C should be 26.8.

These values for the γ's give $F_0 = +0.2$ for octane and $F_0 = -6.2$ dynes per cm for hexadecane. This latter value does not differ greatly from that calculated from Adam's data on the myristic acid films ($F_0 = -13$). The difference is not greater than should be expected because of the uncertain part played by thermal agitation in the spreading of surfaces.

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[8] N. K. Adam, *Proc. Royal Soc.* **A 99**, 336 (1921); **101**, 452, 516 (1922); **103**, 676, 686 (1923); **106**, 694 (1924); *J. Phys. Chem.* **29**, 87 (1925).

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According to Equation (56) with negative values of F_0 the expanded film should not expand indefinitely even if the compressive force F is made negligibly small. Placing $F = 0$ we see that the maximum area covered per molecule will be

$$a_M = a_0 - \frac{kT}{F_0} \tag{58}$$

For the case we have considered where $a_0 = 18$, and $F_0 = -13$, we obtain $a_M = 18+32.3 = 50.3$ A^2 as the maximum area for an "expanded film" of myristic acid on water. This equation shows that the maximum area a_M depends principally upon F_0. By Equation 57 we see that F_0 is the difference between two relatively large quantities which are nearly equal. A very small percentage change in γ_R causes a relatively large change in F_0 and therefore in a_M. As a matter of fact Adam finds that a_M varies only moderately for different substances. As the length of the chain increases he finds a slight decrease in a_M and considers this a strong argument against the view that the molecules tend to lie flat if they have sufficient room to do so. We have seen, however, by our comparison of octane with tetradecane that γ_R and therefore $-F_0$ increase with the length of the chain, and therefore, by Equation (58), a_M should actually increase as the chain is made shorter. The changes in a_M observed by Adam may be accounted for by very small percentage changes in γ_R.

This theory of "expanded films" requires that the molecules remain in contact while Adam concluded that in such films the "molecules become separated and move about independently on the surface" and that "there are spaces not covered by molecules." Adam considered that the *molecules* of the film behaved as a two-dimensional gas while we conclude that it is only the heads of the molecules that behave in this way.

The fact that a palmitic acid film shows no measurable tendency to expand beyond a certain definite area is in accord with the following values of λ which have been calculated from the γ's by the principle of independent surface action.

$\lambda_1 = 181\times10^{-14}$ erg for a molecule oriented vertically in a water surface with the carboxyl group down and surrounded by water molecules except at its upper end which reaches the free surface.

$\gamma_2 = 64\times10^{-14}$ for a molecule lying flat in the surface with the carboxyl group turned downward into the water at one end of the molecule.

$\gamma_3 = 4\times10^{-14}$ for a horizontal molecule at the edge of a film of vertically placed close-packed molecules.

$\lambda_0 = -17\times10^{-14}$ for a vertically placed molecule at the edge of a film of similar vertical molecules.

The difference between λ_4 and λ_1 or λ_2 is so great that according to the Boltzmann equation no appreciable number of molecules can remain isolated in the surface. The few molecules that do exist as separate molecules, however, must all lie flat in the surface because of the great difference between λ_2 and λ_1.

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If we consider lower members of the fatty acid series we find that the difference between λ for the single molecules and for those in clusters becomes much smaller so that separate molecules do exist and therefore the surface tension of water is decreased by even dilute films of these acids in which a, the area per molecule, is very much greater than in expanded films of palmitic acid. The values of λ prove that in such two-dimensional "gaseous" films the molecules lie flat in the surface.

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THE EFFECTS OF MOLECULAR DISSYMMETRY ON SOME PROPERTIES OF MATTER

Colloid Chemistry
Vol. I, 525 (1926).

THE KINETIC theory of gases during the last century led to extremely valuable conceptions and even quantitative laws, notwithstanding the fact that in the development of the theory, it had been necessary to make many simplifying assumptions which frequently were not actually correct. For example, in most derivations it was assumed that the molecules were infinitely hard elastic spheres which acted on one another only at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but for the viscosity, heat conductivity and diffusion of gases, and other phenomena involving the free paths of the molecules. Maxwell, on the other hand, developed a very complete theory based on the assumption that the molecules are point centers of force repelling one another according to the inverse fifth power of the distance between them. This assumption was made not because it was supposed to correspond to the actual forces around molecules, but because it lent itself particularly well to mathematical treatment. The results obtained by Maxwell differed from those based on the assumption of elastic spheres mainly in slight differences in numerical coefficients of the equations obtained. To handle the problem mathematically it was necessary to make assumptions as to the forces between the molecules, but to get most of the essential truths of the kinetic theory it did not much matter exactly what these assumptions were.

To account for the main features of the transition from the gaseous to the liquid state Van der Waals found it necessary to consider attractive forces, but again the particular law of force did not need to be known to obtain this useful result. Sutherland also took into account attractive forces in dealing with the temperature coefficient of the viscosity of gases.

In considering other properties of gases or liquids it may be necessary to analyze the forces around molecules in more detail. For example, Debye (1) showed that the variation of the dielectric constant of a substance with tempera-

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[EDITOR'S NOTE: This paper appears as Chapter Twelve in the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

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ture depends on an orientation of the molecules in an electric field, thus indicating that these molecules are electric dipoles.

W. B. Hardy (2) in discussing the interfacial surface tension between fluids said in 1912:

"If the stray field of a molecule...be unsymmetrical, the surface layer of fluids and solids, which are close packed states of matter, must differ from the interior mass in the orientation of the axis of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways."

In a later paper (3) he adds:

"The surface film must therefore have a characteristic molecular architecture... When the composite surface is formed its architecture is determined by the interaction of the fields of force of molecules of A and B under the influence of the attraction of B for A."

In connection with a study of chemical reactions at the surfaces of highly heated tungsten and carbon filaments in gases at low pressures (less than 0.1 mm) I came to the conclusion (4) that adsorbed carbon monoxide must be regarded as oriented on the surface, so that the carbon atoms are attached to the solid while the oxygen atoms form the surface layer.

Shortly thereafter, without at that time knowing of Hardy's work, I saw the application of these ideas to the orientation of molecules as the surfaces of liquids, and was then able to develop a theory of the effect of chemical constitution on the surface tension of pure liquids as well as solutions and oil films on water.[1]

It is the object of the present paper to consider in a general way the causes of molecular orientation and the effects produced by such orientation on surface tension, solubility, vapor pressure, etc. In particular, since the chemist knows a good deal about the shapes of molecules and the stray fields around their different parts, it will be urged that this knowledge be used to correlate, as nearly quantitatively as possible, the various so-called physical properties which depend on these factors. For this purpose it will not be necessary to have knowledge of the exact shapes and fields of forces of the molecules, but, just as in the case of the kinetic theory, considerable progress may be made even by the crudest kinds of assumptions in regard to these factors.

We know that molecules actually exist and must be of the most varied shapes. Let us therefore consider how the various possible shapes of the molecules and the types of force fields must influence the physical properties of substances.

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[1] A paper on this work was read before the American Chemical Society in September, 1916, and a two-page abstract was published in *Met. Chem. Eng.* **15**, 468 (1916). Before the full work could be published, two papers by W. D. Harkins appeared in *J. Amer. Chem. Soc.* **39**, 354 and 541 (1917), which dealt in detail with the surface tensions of pure liquids. In the final publication of my results, *J. Amer. Chem. Soc.* **99**, 1848 (1917), the part dealing with pure liquids was therefore omitted.

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Types of Interatomic and Intermolecular Forces

The chemical properties of matter are primarily dependent on the number of electrons in the atoms and the manner in which these electrons are able to arrange themselves to form the most stable configurations. The electric forces due to charges on the atoms frequently oppose the formation of certain configurations which, except for these charges, might be the most stable. The effect of these two factors in governing chemical action has been discussed at some length by the writer.[1]

The electron configurations existing in the atoms of the inert gases He, Ne, Ar, etc., are the most stable of all. Other atoms, by taking up, or giving up electrons, or by sharing electrons with each other, strive to obtain electron configurations like those of the inert gases. It is mainly as a result of these changes that chemical interaction occurs.

Each of the ions O^{--}, F^{-}, Na^{+}, and Mg^{++} contains 10 electrons, the same number as in a neon atom. The reason for the formation of chemical compounds containing these ions is that the electrons can thereby become arranged in the stable configuration characteristic of the neon atom.

This view, which is largely that of Lewis and Kossel, and is now generally accepted, may serve as a basis for a classification of intermolecular forces. There are three main types of molecules to consider:[2] (1) Non-polar, (2) Polar, and (3) Ionic, as follows:

1. *Non-polar*

The neon atom, or methane molecule, may be taken as the most extreme example. The center of gravity of the electrons of the molecule coincides with that of the positive charges of the nuclei, so that there is no dipole moment. In general, however, the atom or molecule may behave as an electric quadrupole or system or even higher symmetry. Debye has shown that quadrupole molecules[3] attract one another, when at a considerable distance, with a force which varies inversely with the ninth power of the distances. This result is obtained by considering the deformation of each of two molecules in the electric field of the other. Under the influence of an electric field the electrons become displaced with respect to the nucleus by an amount which may be estimated from the dielectric constant, and thus the molecule becomes polar to a degree which

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[1] "Types of Valence," I. Langmuir, *Science* **54**, 59–67 (1921). The recent work of Bohr, which has proved that the electrons in the heavy atoms (such as niton) are arranged in shells according to the scheme 2, 8, 18, 32, 18, 8 instead of the scheme 2, 8, 8, 18, 18, 32 postulated by the writer, requires only a slight and obvious modification of the wording of Postulate I, and does not otherwise affect the validity of the conclusions that were drawn in that paper.

[2] P. Debye, *Phys. Zeit.* **21**, 178 (1920), has made this classification based on the degree of symmetry of the distribution of electrons within atoms.

[3] The word molecule will be taken to include atoms in those cases where the atoms act as individuals, as, for example, in gaseous or liquid neon.

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depends on the proximity of other molecules. If the molecule is more symmetrical than a quadrupole (as neon probably is), the force will vary inversely with a power of the distance which may be much greater than the 9th.

In general, non-polar molecules do not become oriented in weak electric fields, but when the field becomes very strong, the dipole moment, which may differ for different orientations of the molecule, may cause orientation. However, thermal agitation will nearly always make such orientation negligible for molecules of this type.

2. *Polar*

The molecules of hydrochloric acid gas and water vapor are extreme examples. The center of gravity of all the electrons of the molecule does not coincide with that of the positive charges, so that the molecule acts as an electric dipole. If the separation of the centers of gravity of the electric charges is comparable with the distance between the atoms in a molecule the electric forces are much more intense than in the case of non-polar molecules. The attractive force due to deformation is thus greater than for non-polar molecules. The polar molecules become oriented in an electric field in so far as the thermal agitation will permit. Thus the dielectric constant, or rather that part of it which is due to orientation, varies inversely proportional to the absolute temperature (5). Such orientation of the polar molecules in the field of neighboring molecules, if it occurs to any large degree, causes a very great increase in attractive force between molecules. The amount of orientation increases rapidly as the molecules are brought closer together, and also increases slowly as the temperature is lowered. The force of attraction between two dipole molecules which are oriented in each other's fields is $6e^2\delta^2/r^4$ where e is the charge and δ the displacement of the dipole ($e\delta$ = the electric moment) and r is the distance between the molecules. The force due to orientation thus varies inversely with the fourth power of the distance.

3. *Ionic*

Electrolytic ions such as Na^+, SO_4^{--}, etc., are familiar examples. Gaseous ions must also be included in this group. The molecule, which in this case is an ion, has an unequal number of electrons and protons, or, in other words, the number of electrons is not equal to the positive charges of the nuclei. The electric field around such ions is in general very much greater than around polar and non-polar molecules, and falls off still more slowly as the distance increases. The force between two ions in free space varies inversely as the square of the distance between the ions. But in presence of other molecules, and particularly in presence of other ions, the deformation of the non-polar molecules, the orientation of the polar molecules, and the concentration differences among the ions all tend to decrease the forces between ions. The increased concentration of positive ions around negative ions and *vice versa* causes the force

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between two given ions to decrease with increasing distance more rapidly than according to the inverse square law. Debye and Hückel (6) have recently been able to develop a mathematical theory of these effects which has cleared up at one stroke most of the perplexing problems involved in the theory of electrolytic dissociation.

Attractive Forces

From this analysis we see that there are three fundamental factors that cause attractions between molecules:

a. Deformation
b. Orientation
c. Segregation

Debye has shown that two uncharged molecules, each consisting of a *rigid* structure of positive and negative particles, would on the average exert no force on one another if all orientations of the molecules are equally probable. But, since all substances have dielectric constants greater than unity, the particles must become deformed when they get into each other's fields. This deformation is always such as to cause an attraction between the molecules.

In general, there will also be a tendency for molecules to be oriented when they approach one another sufficiently closely. This orientation always increases the attractive force.

Debye has also pointed out that if, around a given ion in an electrolyte, there were no concentration of ions of opposite sign, there would be no resulting attraction between an ion and its neighbors. But since there is in fact around any ion an increased concentration of ions of opposite sign, there is a resulting attractive force which opposes the osmotic pressure of the ions, due to their thermal agitation. It is this effect which we have denoted by the term *Segregation*. It may occur not only with ions, but also with dipole molecules such as those of water. By the segregation of dipole molecules and their orientation about a given molecule or ion electric forces may be transmitted through distances larger than would otherwise be possible.

Repulsive Forces

Of course the attractive forces in matter must be balanced by equal repulsive forces. Very little has been definitely known about these forces except that they vary inversely with some very high power of the distance between molecules. In the past in the kinetic theory it has been usual to take into account these repulsive forces merely by assuming that the molecules behave like infinitely hard elastic spheres which is equivalent to assuming that the force varies inversely with an infinite power of the distance.

In order to account for the compressibility of solids Born and Landé (7) have shown that definite exponents for the repulsive force must be assumed. Thus in the case of halide salts of the alkalis such as NaCl, KI, etc., he showed that

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the compressibility of the solid salts indicated that the repulsive force varied inversely as the 10th power of the distance between the ions, while the attractive force varied inversely as the square of the distance in accord with Coulomb's Law. Born (7a) also attempted to show that the inverse 10th power law for repulsion could be *deduced* by assuming that the electrons in the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. 1st. The method of mathematical expansion used is not legitimate when applied to distances as short as those between ions in salts, and 2nd, Born assumed that the cubical ions were all oriented so that their edges are parallel. This kind of orientation would be unstable under the forces assumed. If the atoms should become oriented in response to the forces acting, the repulsive force would disappear and would be replaced by an attractive force which would act in addition to the force between the ionic charges.

Such orientation of ions as Born assumes may very possibly exist in solid crystals from causes which he does not discuss, but this orientation cannot be the cause of the repulsive forces which determine the compressibility, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility, whereas by the reasoning of Born's theory the repulsive forces, being then unbalanced, should cause a complete collapse of the structure.

Thus we cannot regard Born's theory as one that throws any light on the cause of the repulsive forces.

Debye (8), however, has recently developed a theory which seems to indicate the nature of the repulsive forces. It depends essentially on the orbital motions of the electrons within the atoms in accord with Bohr's theory, whereas Born in his calculations had assumed that the electrons acted as if stationary. Debye assumes that the conditions imposed by the quantum theory determine the size of the electron orbits and the frequency of rotation in these orbits. Thus the electric field around an atom or molecule is not a static field but is a pulsating or partly oscillating field increasing in amplitude of oscillation very rapidly as the surface of the atom is approached. Thus when an electron approaches an atom it acquires in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom, the resulting force will be one of repulsion. This repulsive force may be assumed to exist not only for free electrons but for electrons which themselves are involved in the orbital motions of other atoms.

Thus the repulsive forces between atoms and molecules are due to the perturbations in the electron orbits caused by the motions of the electrons which revolve in orbits in neighboring atoms. The repulsive force does not originate from an atom as a whole, but comes from the close approach of electrons in

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the two atoms. Thus we should look upon these forces as surface forces and should try to express them as functions of the distances between the surfaces of the atoms (fixed by the outer electron orbits rather than in terms of the distances between the centers of the atoms.

Forces at the Surfaces of Molecules

In a discussion of the compressibility of metals and its relation to interatomic forces (9) the writer has shown that the range of the attractive forces between the atoms is approximately the same for all metals, although the compressibilities of the metal and the volumes of the atoms vary over wide ranges. Thus although the compressibility of caesium is 220 times that of tungsten, and the atomic volume is 7.4 times that of tungsten, the range of the attractive force is nearly the same, 0.66×10^{-8} and 0.57×10^{-8} cm respectively.

Debye (10) in a paper of 1920 in analyzing the causes of attractive forces between non-polar molecules attempts to calculate the force from assumed stationary electron configurations. For this purpose he expressed the electric potential in the neighborhood of a given molecule in terms of an infinite series expanded according to reciprocal powers of the distance r from the center of the molecule. If the molecule is uncharged (i.e., is not ionic) the first term which involves $1/r$ vanishes. If the molecule is non-polar (i.e., has no electric dipole moment) the second term involving $1/r^2$ vanishes. For a nonpolar molecule, which is of the type of a quadrupole, the third term is therefore the first term which does not vanish. Debye considers therefore the effects due to this term involving $1/r^3$ and ***neglects all subsequent terms in the series.*** If, however, the molecule has a higher degree of symmetry than that of a quadrupole (for example a tetrahedron or cube) the third term (which is the only one that Debye considers) should also vanish.

Debye then calculates that the average force which acts on a molecule B when at a distance r from a similar molecule A is given by

$$F = \frac{24at^2}{r^9} \tag{1}$$

where t is a function only of the "electric moments of inertia" (Σex^2, Σey^2 and Σex^2) determined by the positions of the electrons and nuclei in the molecule. The quantity a measures the deformability or ease of polarization of the molecule in an electric field and can be calculated from the dielectric constant, or better from the molecular refractive index.

Debye then proceeds to test these conclusions by calculating from this equation the coefficient a in the van der Waals' equation.

$$\left(p+\frac{a}{V^2}\right)(V-b) = RT \tag{2}$$

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which measures the attractive forces between molecules. He finds

$$a = \frac{6\pi}{5}\frac{N^2\alpha\tau^2}{d^5} \tag{3}$$

where N is the Avogadro constant (6.06×10^{23}) and d is the diameter of the molecule. In deriving this relation Debye assumes that the force between the molecules is given Equation by 1 for all distances from d to ∞. Considering the derivation of Equation (1) it is clear that we have no right to apply it to distances comparable with the diameter of the molecule, for the neglected terms in the expansion on which it is based, should then be as important as the term actually considered. Debye, however, uses Equation 3 to calculate τ from the experimentally determined values of a.

He then compares the values of τ obtained in this way with those calculated by another method from the Sutherland constant c which is determined from the temperature coefficient of the viscosity η of gases by the equation

$$\eta = \frac{\text{const}\sqrt{T}}{1+\frac{C}{T}}$$

The Sutherland constant is a measure of the attractive forces between molecules and thus Debye is able to express it in terms of τ which occurs in Equation 1.

The values of τ calculated by these two independent methods agree very well with one another (average error about 4 per cent) for the gases argon, krypton, xenon, nitrogen, oxygen and ethylene which have molecules of the non-polar type. For hydrogen and helium, however, the errors are about 50 per cent. Debye concludes that this good agreement indicates that "the law of force (Equation 1) and its interpretation correspond completely to reality." Undoubtedly the agreement justifies the use of the inverse 9th power law of attractive force between non-polar molecules and the relation between the attractive forces and the refractive index, but it should not be concluded that this is evidence of the correctness of the relation between τ and the assumed arrangement of electrons (electric moment of inertia).

With a force which varies with the inverse 9th power, the force falls to one-half value for an increase of only 8 per cent in the distance. Thus the cohesive forces corresponding to the van der Waals and Sutherland constants are determined mostly by the forces exerted by the molecules upon one another during the times that their distance apart does not exceed the distance of minimum approach by more than 10 per cent.

When a molecule is as close as this to another the force acting at the near side of the first molecule would be about 10,000 times as great as the further side of the molecule. We are then surely not justified in considering that the deformation would be the same as if the molecule were in a uniform field

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having the intensity of that at the center of the molecule. The fact that Debye does get good agreement must be due to two compensating errors. 1st the field at the near side of the molecule where it alone needs to be considered is much stronger than that calculated by Debye, and 2nd this field acts effectively on only a small part of the molecule and its effect is thus reduced.

Examining Debye's data we find that the values of τ which he finds are quite accurately proportional to the 4th power of the molecular diameter. From this it can be shown that the root-mean square electric field at the surface of the molecule which causes the mutual polarization of the molecules when they are in contact is practically the same for all the substances considered, and has the value of 9.8×10^{8} volts per cm (for $r = d$) which is the field that exists at a distance 1.21×10^{-8} cm from an electron.

Thus we see that the intensities of the fields around different non-polar molecules are practically identical when regarded as surface forces rather than as forces which originate at the center of the molecules.

Surface Forces as the Cause of Molecular Orientation

The surface tension γ of a liquid is the free energy per unit area or is that part of the surface energy which can do work. The total energy per unit area γ_0 is given by

$$\gamma_0 = \gamma - T\frac{d\gamma}{dT} \tag{4}$$

To produce isothermally a new surface of unit area we must expend the work γ, but the total energy increases by more than this, the difference $-T(d\gamma/dT)$ being derived from heat energy, and thus causing a cooling effect.

In general the temperature coefficient $d\gamma/dT$ is practically constant, and therefore by Eq. (4) γ_0 is constant and equal to the value of γ at $T = O$. From the linear change of γ with temperature it is probable that the variation of γ is a direct result of the thermal agitation of the molecules, and is not due to any change in the structure of the surface. In studying the effects of molecular orientation we must, therefore, consider the total energy γ_0 rather than the free energy.

In the early work on the orientation of the molecules in the surfaces of organic liquids, the writer pointed out that the different portions of the molecules produced their characteristic effects independently of the presence of the other portions of the molecular surface. Thus it was stated (11):

"The surface energy of a liquid is not a property of the molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer. In liquid hydrocarbons of the paraffin series the molecules arrange themselves so that the methyl groups at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same no matter how long the chain may be. As a matter of fact the surface energies of the hydrocarbons from hexane to molten paraffine,

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have substantially the same surface energy (46–48 ergs per cm^2) although the molecular weights differ very greatly. If we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies are practically identical with those of the hydrocarbons*. The reason for this is that the surface layer in both cases consists of CH_3 groups."

We see that this conception of surface forces is in agreement with the conclusions that we have reached by our more general considerations of intermolecular forces. We may, however, use this idea of separate surface energies for different parts of the molecular surface, to explain the orientation of the molecules and many other phenomena observed in liquids.

Let us apply the idea of surface energy to the surface of a molecule in the same manner as we apply it to a large surface of a liquid. As an example we will consider a molecule of palmitic acid, $C_{15}H_{31}COOH$ and calculate the difference in surface energy when the molecule is in various environments. From the density 0.85 and the molecular weight 256 the volume per gram molecule is 301 cm^3 and from the Avogadro number we find the volume per molecule to be 497×10^{-24} cm^3. Because of surface tension forces a molecule of palmitic acid vapor will assume a nearly spherical form in which the carboxyl group is buried as completely as possible within the sphere. Thermal agitation and internal stresses in the molecule will tend to prevent the molecule from being truly spherical, but with a molecule as large as palmitic acid the effect of the surface energy should predominate and make the molecule approximately spherical. Let us estimate the maximum and minimum surfaces which the molecule may possess.

The minimum surface will correspond to the spherical form. The diameter of a sphere having a volume[1] of 497 A^3 is 9.83 A and its surface is 304 A^2. The maximum area occurs when the hydrocarbon chain is as nearly straight as possible. The experiments on adsorbed films on water have shown a minimum cross-section of 20 A^2 for the hydrocarbon chain. If we consider the molecule to be a cylinder having this cross-section and having hemispherical ends, we find the diameter to be 5.04 A, the length of the cylindrical part 21.5 A and the total surface 420 A^2, which is 39 per cent greater than the surface when the molecule is spherical.

The difference in surface (116 A^2) multiplied by the surface energy of hydrocarbons (50 ergs per cm^2) gives the energy involved in the transformation between the cylindrical and the spherical form.

Let us then consider whether this energy of 58×10^{-14} ergs is sufficient to cause the molecule to assume a nearly spherical form.

The ratio P_1/P_2 of the probabilities of the occurrence of any particular configuration of a molecule is given by the modified Boltzmann equation

$$\frac{P_1}{P_2} = \frac{p_1}{p_2} e^{-\frac{\lambda}{KT}} \tag{5}$$

[1] For convenience we shall express molecular dimensions in terms of the Ångstrom unit 10^{-8} cm; thus 5 $A^2 = 5 \times 10^{-16}$ cm^2 and 4 $A^3 = 4 \times 10^{-24}$ cm^3 [A stands for Å.U. J.A.]

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where λ is the energy required to change the molecule from the state 2 to state 1, and p_1 and p_2 are the *a priori* probabilities of the two states, which are largely determined by geometric factors and the definitions of the two states. If we put $\lambda = 58 \times 10^{-14}$, $T = 293$, the exponent is -14.4 and the exponential factor is thus 6×10^{-7} so that nearly all the molecules must be in a nearly spherical form unless p_1/p_2 has a very large value. If the surface energy λ were zero the ratio p_1/p_2 would measure the relative probabilities of the two configurations. Of course the probability p_2 would be zero if we were to consider only absolutely spherical molecules. We should therefore consider a range for each state, taking, for example, state 2 to be one in which the surface area is not more than 5 per cent greater than that of a perfect sphere, while state 1 is one in which the area is not less than 95 per cent of that of the cylindrical molecule already considered.

If λ were zero, thermal agitation would make the molecules assume the most varied shapes. It seems likely, however, that in most of these configurations there will be a relatively large part of the surface of the hydrocarbon chain exposed, so that p_1 will be larger than p_2. But this difference in probabilities will be a very moderate one, not at all able to compensate for the very small value of the exponential factor in Equation (5) when λ has the value 58×10^{-14} erg.

In these calculations we have used the total surface energy γ_0 instead of the free energy. The thermal agitation may tend to oppose the contraction of the surface of a single molecule, but probably to a much smaller extent than in the case of a large surface of many molecules. However, the conclusion that there is ample energy to bring about a nearly spherical form would not be altered if λ were half as great as we found, so that for the present we shall not attempt to draw a distinction between free energy and total energy in applying Equation (5).

If a palmitic acid molecule is surrounded by water, the hydroxyl group is nearly completely surrounded by water molecules, while the hydrocarbon chain will draw itself as nearly as possible into a sphere, since the interfacial surface energy between water and hydrocarbon is about 59 ergs, which is even more than the surface energy of a hydrocarbon (against vapor).

Before proceeding with the properties of the palmitic acid molecule let us consider the somewhat simpler problem of a hydrocarbon molecule. To facilitate comparison we will assume that the hydrocarbon molecule has the same volume (497 A^3) as the palmitic acid molecule. This corresponds approximately to hexadecane $C_{16}H_{34}$. Let us now calculate the energy needed to transfer such a molecule from a hydrocarbon liquid to: 1. the interior of a mass of water; 2. a vapor phase, and 3. an adsorbed film on the surface of the water.

While the hydrocarbon molecule is in a liquid consisting of other (saturated) hydrocarbons its surface energy may be taken to be zero, since there

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are no interfaces, even if the surrounding hydrocarbon molecules are of different molecular weight. When the molecule is transferred to the interior of a large volume of water the surface energy is $\lambda = s\gamma_0$ where s, the surface of the molecule, is 304 A^2 and the interfacial surface energy $\gamma_0 = 59$ ergs per cm. Hence $\lambda = 179 \times 10^{-14}$ erg. For the formation of a molecule of vapor we have the same value of s but $\gamma_0 = 50$ so that $\lambda = 152 \times 10^{-14}$.

These energies correspond respectively to the heat of solution and the heat of evaporation of the hydrocarbon molecule. Actually the heat of evaporation is about 55 per cent of the value calculated in this way. The agreement as to order of magnitude is satisfactory. The surface energy 50 ergs per cm^2 is that which is measured when a fraction (probably about 1/3) of the surface of the molecules is exposed, while the heat of evaporation corresponds to the whole surface exposed. It is probable that the difference is caused by the more unsymmetrical state of the molecule when only part of its surface is exposed and by the resulting increase in the surface energy or stray field.[1]

From the fact that λ for the hydrocarbon molecule in water or in the vapor state is so large we may conclude from the Boltzmann equation that the vapor pressure and the solubility are very small in the case of a hydrocarbon with a molecule as large as we are considering (16 carbon atoms). With lower molecular weights the surface area of the molecules becomes less and the volatility and solubility thus increase. The relatively small solubility of even the lower hydrocarbons may be explained in this way.

The energy of transfer of a hydrocarbon molecule to an adsorbed film on water will depend on the configuration and the orientation of the molecule in the surface. Let us consider three possible cases:

(*a*) A spherical molecule half immersed in the water. The energy λ is thus the sum of the energies of the two hemispherical surfaces minus the energy of the water surface which is destroyed by the presence of the hydrocarbon molecule. The cross-section of the molecule through the center is 76 A^2 while each hemisphere has a surface of 152 A^2. Taking the total surface energy of water to be 117 ergs per cm^2 we have

$$\lambda = (59 \times 152 + 50 \times 152 - 117 \times 76) 10^{-16}$$
$$= 77 \times 10^{-14} \text{ ergs.}$$

(*b*) A cylindrical molecule, half immersed in the water, oriented with its axis parallel to the water surface. The area of the section parallel to the axis is 128 A^2 and half the molecular surface is 210 A^2 so that

$$\lambda = (59 \times 210 + 50 \times 210 - 117 \times 128)\ 10^{-16}$$
$$= 79 \times 10^{-14} \text{ erg.}$$

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[1] In a paper to be published in the *Journal of Physical Chemistry* this theory of evaporation is developed and discussed in more detail and gives quantitative agreement with the heats of evaporation not only of hydrocarbons, but of alcohols and other substances.

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(*c*) A cylindrical molecule, half immersed in the water, oriented with its axis perpendicular to the water surface. The cross-section of the molecule parallel to the water surface is 20 A². Thus we have

$$\lambda = (59\times 210+50\times 210-117\times 20)\ 10^{-16}$$
$$= 206\times 10^{-14}$$

Table I gives a summary of these results to facilitate comparison.

TABLE I

Surface Energy of a Hydrocarbon Molecule $C_{16}H_{34}$ *Having a Volume* 497 A³

Sphere 9.83 A diameter 304. A² surface or Cylinder 5.04 A diameter 420. A² surface

Location of molecule	Shape and orientation of molecule	Energy in erg $\times 10^{-14}$
In liquid hydrocarbon	Sphere or Cylinder	0
In water	Sphere	179.
	Cylinder	248.
In vapor	Sphere	152.
	Cylinder	210.
Adsorbed on water (half immersed)	Sphere	77.
	Horizontal cylinder	79.
	Vertical cylinder	206.

Surface energies used in calculations—water vs. vapor 117, water vs. hydrocarbon 59; hydrocarbon vs. vapor 50 ergs per cm as taken from tables by Harkins *et al.*

The difference in energy between the spherical and cylindrical form when the molecule is in the vapor phase or the water phase is so great that the molecules will be nearly spherical. But with the molecule in the interface the difference in energy (2×10^{-14}) between the sphere and the horizontal cylinder is so small that it will have little effect in determining the shape, the exponential factor in Equation 5 being only 0.61. Thus the configuration of the molecule will depend almost wholly on the *a priori* probabilities. For reasons already given a nearly spherical form is improbable as compared to an extended or irregular form in which the larger part of the molecule is exposed. These considerations lead us to conclude that a hydrocarbon molecule adsorbed on a water-surface will lie flat on the surface when not crowded by other adsorbed molecules.

This conclusion is the same as that reached by the writer from a study [12] of the surface tensions of dilute solutions having non-saturated adsorbed films.

The very high value of λ in the case of the vertical cylinder shows that molecules can be oriented vertically only very rarely. The difference in energy be-

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tween the horizontal and vertical cylinder (127×10^{-14}) gives, when substituted in Equation (5), an exponential factor of 2×10^{-14}. In this case the *a priori* probabilities of the two orientations are the same so that only one adsorbed molecule out of about 10^{14} will be oriented in a vertical direction.

The energy 79 corresponding to the adsorbed molecule is very much less than the 152 for the vapor or 179 for the water phase. We can thus see that the presence of molecules in the interface is very much more probable than in either the water phase or the vapor. This conclusion is strikingly in accord with the facts.

Hexane vapor coming into contact with water lowers its surface tension very considerably. According to Gibbs' Law this proves that there is an adsorbed film of hexane molecules in the surface having a much higher concentration than that of either the vapor phase or the water phase. With hexane the energy of transfer to the adsorbed film is roughly about 6/16 ths of that for hexadecane but the ratio of this energy to that in the vapor or water phase is about the same for the heavier molecule. As the length of the chain increases the vapor pressure, solubility and amount of substance adsorbed decrease, but the ratio of the amount adsorbed to that in either phase must increase.

We shall see that this is the fundamental cause of the formation of monomolecular films of organic substances on water. The *ratio* between the concentration of the substance in the film and in the water is not greatly altered by the presence of an active group (such as carboxyl) in the molecule. The principal effect of the active group is to increase the solubility of the substance in water and therefore cause a corresponding increase in the amount adsorbed.

The Effect of an Active Group

When we replace a hydrogen atom in a hydrocarbon by a hydroxyl, carboxyl or similar radical we change the surface energy of a part of the molecule very greatly without having very much effect on the remainder of the molecular surface. From this viewpoint we have at once an explanation of the fact that the introduction of such a radical or active group lowers the vapor pressure and increases the solubility.

Let us now take up again the consideration of the palmitic acid molecule as an example of a molecule having an active group. We shall adopt Adam's terminology and refer to the hydrocarbon portion of the molecule as the tail and to the active group — COOH as the head. Representing the molecule by the usual symbol RX we shall thus let R denote the tail and X the head. For the calculations of the surface energies we shall adopt the following values for the surface energies (ergs per cm²).

$$\gamma_R = 50 \qquad \gamma_{RW} = 59$$
$$\gamma_X = 144 \qquad \gamma_{RX} = 20$$
$$\gamma_W = 117 \qquad \gamma_{XW} = -30$$

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The subscript w refers to water. The surface energies of hydrocarbons and of water, γ_R and γ_W respectively are the values we have already used and are those given by Harkins for the liquids in bulk. The same is true for the interfacial energy γ_{RW}. The value of γ_X has been obtained from a study of heats of evaporation of hydrocarbons and fatty acids while γ_{RX} and γ_{XW} were found from a study of the vapor pressures of binary mixtures by a method which we shall soon describe briefly. The negative value for the surface energy between carboxyl and water which results from these studies is in accord with the very marked increase in the solubility in water caused by the presence of this group.

We have already estimated the surface area of the palmitic acid molecule, but we now need to know the surface of the carboxyl group. From a comparison of the volumes of the molecules of the lower fatty acids we may estimate the surface to be 45 A^2 which is the value that was assumed in obtaining the values of γ_X, γ_{XR} and γ_{XW}.

Table II gives the dimensions of palmitic and butyric acid molecules calculated from the molecular volumes assuming three different shapes. The hydrocarbon tail is taken as spherical, cylindrical or of the form of a hexag-

TABLE II

Dimensions of Palmitic and Butyric Acid Molecules

	Palmitic acid $C_{15}H_{31}COOH$	Butyric acid C_3H_7COOH
Molecular weight	256.	88.
Density	0.85	0.96
Volume per molecule	497. A^3	150. A^3
Sphere		
Diameter	9.83 A	6.59 A
Total surface	304. A^2	136. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	259. A^2	91. A^2
Section of tail	76. A^2	34. A^2
Cylinder with Hemispherical Ends		
Diameter	5.04 A	5.04 A
Length of cylindrical part	21.50	2.80
Total surface	420. A^2	146. A^2
Surface of head	45. A^2	45. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	375. A^2	101. A^2
Transverse section of tail	20. A^2	20. A^2
Longitudinal section of tail	108. A^2	34. A^2
Hexagonal Prism		
Side of hexagon	2.64 A	2.64 A
Total surface	420. A^2	146. A^2
Transverse section	20. A^2	20. A^2
Longitudinal section	108. A^2	34. A^2

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onal prism, this latter shape being useful when considering molecules packed in surface films.

The surface energies of these molecules in various environments have been calculated from the data in Table II by means of the assumed values of the γ's and the results are given in Table III. The assumed locations and orientations are illustrated diagrammatically in Fig. 1, in which the numbers correspond to those in the first column in Table III. The relative lengths and diameters shown in Fig. 1 agree with those given for palmitic acid in Table II except that the molecule marked 6b illustrates the butyric acid molecule in a cylindrical form.

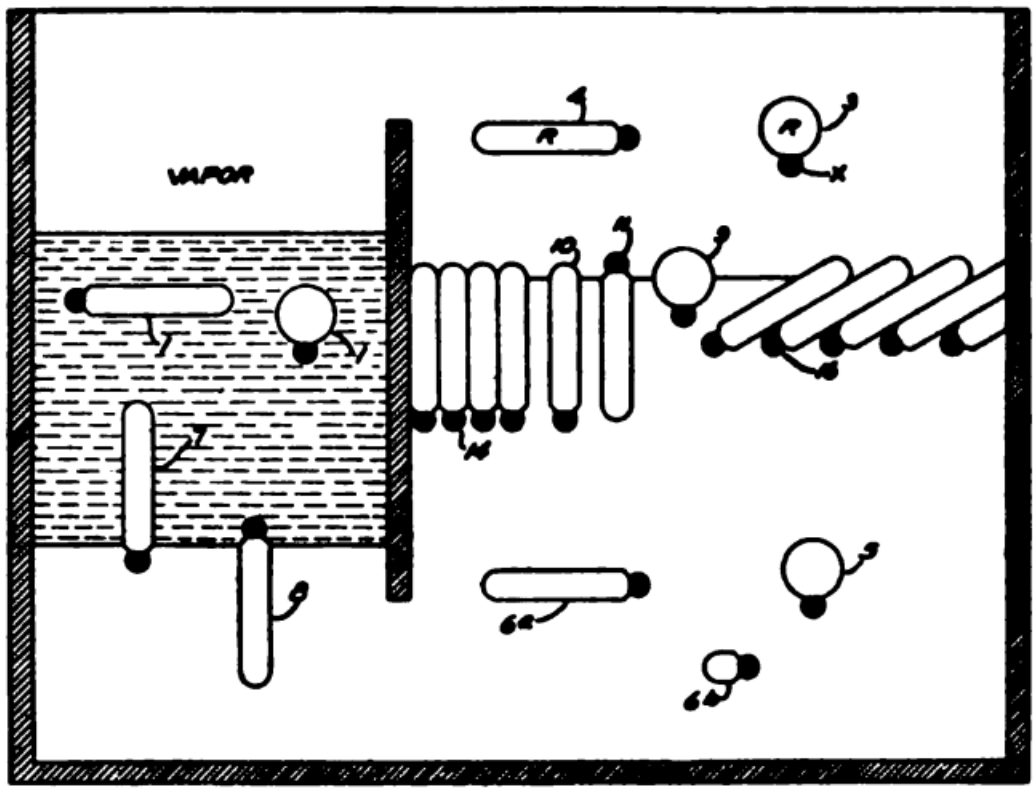

FIG. 1. Diagram illustrating the various locations and environments of molecules considered in Table III.

As an example of the method of calculating the surface energy let us consider Case 10 in which a molecule of palmitic acid is adsorbed on a water surface. The hemispherical upper end of the molecule which extends above the water has a surface of 40 A^2 and since the surface energy γ_R is 50 this part of the molecule contributes 20×10^{-14} erg. The surface of the chain in contact with the water is $375-40 = 335$, and the surface of the head is 45. The surface of water destroyed by the presence of the molecule is 20, so that the total energy, obtained by multiplying these surfaces by the corresponding γ and adding is $(40\times50)+(335\times59)+(45\times-30)-(20\times117) = 181\times10^{-14}$ erg.

In Case 2 where we consider a palmitic acid molecule in liquid palmitic acid we assume a random distribution of the molecules of the liquid. Each molecule has a tail having a surface of 375 while the surface of the head is 45, the head thus occupying 10.7 per cent of the whole surface. Considering the tail of a given molecule, we thus conclude that 0.107 of 375 or 40.2 is the area of the tail in contact with the heads of neighboring molecules while the remainder of the tail is in contact with other tails and therefore has no surface energy. Similarly we see that 0.107 of 45 or 4.8 is the area of the head in contact with

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other heads, while the remaining 40.2 of surface is in contact with tails. Thus the surface energy $2\times40.2\times20\times10^{-16} = 16.1\times10^{-14}$ erg is associated with the molecule we are considering. Only half of this energy, however, can properly be attributed to this molecule for if these interfaces are destroyed by removing the molecule (leaving a cavity) half the energy in question (viz.

TABLE III

Surface Energies of Palmitic Acid and Butyric Acid Molecules in Various Environments (*See Fig.* 1)

Case No.	Location of molecule	Shape and orientation	Surface energy	
			Palmitic acid -10^{-14} Erg	Butyric acid -10^{-14} Erg
1.	In liquid hydrocarbon	Sphere or Cylinder	9	9
2.	In its own liquid (palmitic or butyric)	Cylinder	8	6
3.	In vapor phase (head exposed)	Sphere	189	111
4.	,, ,, ,, ,, ,,	Cylinder	252	115
5.	In water	Sphere	139	40
6.	,, ,,	Cylinder	208	46
7.	At interface between water and hydrocarbon	Cylinder, vertical, X down	−37	−37
8.	At interface between water and hydrocarbon	Cylinder, vertical, X up	207	45
9.	Adsorbed on water surface (single molecules)	Sphere (half immersed)	39	−4
10.	Adsorbed on water surface (single molecules)	Cylinder, vertical, X down	181	19
11.	Adsorbed on water surface (single molecules)	Cylinder, vertical, X up	236	74
12.	Adsorbed on water surface (single molecules)	Prism, horizontal	64	1
13.	Adsorbed at edge of film	,, ,,	− 4	− 8
14.	,, ,, ,, ,, ,,	,, vertical	−17	−17
15.	,, in single vacancy in film	,, horizontal	−78	−32

8×10^{-14}) can be recovered by allowing the cavity to collapse. Thus 8×10^{-14} erg represents the surface energy of a palmitic acid molecule when surrounded by similar molecules.

Case 14 deals with a molecule oriented vertically at the edge of a surface film of similarly oriented molecules. The molecules are assumed to be hexagonal prisms arranged like the cells in honeycomb. On the average each new molecule added to the edge of the film makes contact with the molecules already present on three of the six faces of the prism. Three of the old faces are thus

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destroyed and three new ones are produced so that the lateral area of the edge of the film (whether in contact with vapor or water) is not altered by the presence of a new molecule. The change in surface energy due to the new molecule is thus:

1. The energy of the upper end in contact with vapor. This area may be estimated as $30 \times A^2$ so that the energy is $30 \times 50 = 15 \times 10^{-14}$.

2. The energy of the head in contact with the water. We may assume that the area 30 A^2 is in contact with the water while the remaining 15 A^2 of the head is in contact with the adjacent heads. This energy is thus $30 \times -30 = -9 \times 10^{-14}$.

3. The energy due to the water surface destroyed which is $-20 \times 117 = -23.4 \times 10^{-14}$.

The total energy of a palmitic acid molecule at the edge of a film is thus $15 - 9 - 23.4 = -17.4 \times 10^{-14}$ erg.

In Case 13 the new molecule at the edge of the film is assumed to lie horizontally being in contact with the other molecules of the film only over one of its six faces.

Case 15 deals with the change in energy when a molecule is removed from a surface film of horizontally packed molecules (not at its edge) so as to leave a vacancy.

An examination of the surface energies λ of the molecules in various environments as given in Table III shows that they explain many of the properties of these substances. The small difference between λ in Cases 1 and 2, being less than the value of kT (4×10^{-14} erg at ordinary temperature), indicates that both palmitic and butyric acids should be miscible with hydrocarbons in all proportions.

It is of interest to note that the difference between λ for a molecule in a hydrocarbon and in its own liquid increases as the chain becomes shorter. An example of an effect of this kind, sufficient to lead to relative insolubility, is observed in the case of methyl alcohol which is miscible with hexane in all proportions only at temperatures above 43°C.

The solubility of palmitic acid in water is immeasurably small while butyric acid mixes with water in all proportions at temperatures above −2.5°C. These facts are in general accord with the values of λ given under Case 5. Comparing these with the values for the corresponding hydrocarbons (Table I) we see that the introduction of the carboxyl group lowers the value of λ by 40 units. This accounts for the great increase in solubility.

Comparing Cases 5 and 6 we conclude that the tail of the palmitic acid molecule in water must assume a nearly spherical form while with the butyric acid molecule, thermal agitation will be able to cause the tail to spread out as a chain.

The most interesting applications of the data in Table III are in connection with the arrangements of molecules in surface films. Comparing Cases 2, 5, 7 and 8 we see that the decrease in energy corresponding to Case 7 is so great

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that practically no molecules could exist in either a water phase or a hydrocarbon phase until the interface becomes saturated with molecules which are all oriented with their heads in the water phase. The relative number of molecules having this orientation as compared to those having the reverse orientation (Case 8) is found from the Boltzmann equation to be as 10^{26}:1 for palmitic acid and 10^{9}:1 for butyric acid.

In a similar way we may estimate the probabilities of the various possible orientations of molecules adsorbed at the free surface of water. The high value of λ in Case 11 in which the molecule is oriented vertically with the carboxyl group uppermost shows that no molecules can be in this position.

Without such analysis as we are now making it might seem that single molecules of palmitic acid adsorbed on the surface of water would take up a vertical position as is illustrated in Case 10, the carboxyl group being downwards. In fact N. K. Adam as one result of work described in a series of valuable papers (13) concludes that "expanded films are two-dimensional gases"[1] in which there is considerable space vacant between the molecules and that in these films "the molecules are oriented perpendicular to the water surface."[2] An examination of Table III shows, however, that the value of λ corresponding to this orientation has the high value of 181, while for a molecule lying flat in the water surface (with the carboxyl group turned downward into the water at one end of the molecule) λ is only 64 (Case 12). A slightly lower energy ($\lambda = 39$) is calculated (Case 9) for spherical molecules half immersed in the water surface. But the *a priori* probability of the spherical form (particularly in case of butyric acid) is so much less than that of the spread-out form of a molecule which lies flat, that this latter form becomes the more probable.

This conclusion that the hydrocarbon chains of adsorbed molecules lie flat in a water surface was reached by the writer in 1917 (14) from a study of Taube's and Szyszkowski's data on the surface tensions of dilute aqueous solutions of fatty acids and other aliphatic compounds. The energy change involved in the transfer of a $-CH_2$ group from the interior of the solution to the surface was found to be constant and equal to 625 calories per gram molecule or 4.3×10^{-14} erg per molecule.

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[1] See paper by G. Friedel, *Colloid Chemistry*, Chemical Catalog Co., 1926, p. 102. Some of the structures he describes may be one or two dimensional solids. J. A.

[2] In a footnote in his last paper Adam rejects the suggestion that I had made to him that the molecules in expanded films tend to lie flat on the water surface becoming overlapped if sufficiently crowded. He says "There is the more probable alternative, however, that as soon as the molecules have separated, through expansion of the films, they sink in among the water molecules so as to satisfy the attractive forces of the chains. If this is so they will probably remain vertical. Nevertheless it must be remembered that the pressure in two dimensions in the surface is only about one sixth of that expected from the gas laws, and no satisfactory explanation of this fact is at present available." The analysis in the present paper shows that a sinking of the molecules does not satisfy the attractive forces, but that the hydrocarbon chains must be in contact with one another whenever possible, otherwise they must lie flat in the surface.

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By Table III the difference between λ for palmitic and for butyric acids, due to the 12 CH_2 groups, is 63 for horizontal molecules on water, while for molecules in solution it is 162 for cylindrical and 99 for spherical molecules. Thus the energy of transfer from the interior to the surface is 8.3×10^{-14} for each CH_2 if the molecule in water is cylindrical and 2.8×10^{-14} if it is spherical. The value 4.3×10^{-14} found from the 1917 work lies between these values and is thus consistent with the results given in Table III.

In discussing the spreading of adsorbed films of the higher fatty acids on water and in comparing these films with those of the lower fatty acids, it was pointed out in the 1917 paper that the films produced by small concentrations of the lower acids behaved like two-dimensional gases obeying the gas law

$$Fa = kT. \tag{6}$$

Here F is the spreading force (dynes per cm) and a is the area (in cm²) per adsorbed molecule. It was found that

"in the case of the higher fatty acids the films do not spread upon the surface in the way required by this equation. Thus with palmitic acid the force F falls to 0.2 dyne per cm when $a = 23$ A whereas by the equation the force should be 17.5 dynes per cm for this value of a.

"Any solid or liquid film must have a certain tendency to spread on the surface by giving off separate molecules which follow the gas laws. This tendency may be measured as a 'surface vapor pressure'. With palmitic acid and higher fatty acids this pressure is less than 0.1 dyne per cm. The smallness of this pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapor phase and from going into solution in the water. There are thus initimate relationships between the lowering of surface tension produced by fatty acids and the vapor pressures and solubilities of these substances. These relationships will be discussed in more detail in another part of this paper."

It was intended to publish the work here referred to as Part III of the paper on the Constitution and Fundamental Properties of Solids and Liquids, but war work which began at that time prevented the carrying out of this plan. The present paper, however, deals with this subject in the manner that was then contemplated.

It was also shown in the 1917 paper that a film of palmitic acid on water at 16°C resists compression with a force greater than 1 dyne per cm only when a, the area per molecule, is less than 21 A². But if the water is heated to 45° the film resists compression when a is 33 A² and a similar value of a is found at 16° if a very small amount of acid is added to the water. Thus adding acid or raising the temperature causes the film to expand if the applied compressional force is not over 10 or 20 dynes per cm. Adam has called such films "expanded films". He believes, as we have seen, that the molecules in these films are in the condition of a two-dimensional gas and that the molecules are oriented vertically. Let us see what light is thrown on these questions by the calculations of Table III.

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A palmitic acid molecule at the edge of a film of vertically close-packed molecules has an energy $\lambda = -4$ if the molecule is horizontal (Case 13) and $\lambda = -17$ if the molecule is vertical (Case 14) like those in the rest of the film. Thus the vertical orientation is the more probable. An isolated molecule lying flat in the surface (Case 12) gives $\lambda = 64$. The difference 81 is so great that the conclusion may be drawn that practically no molecules will exist isolated in the surface layer but that they will all exist in clusters in which the molecules have their hydrocarbon chains in contact with each other. These values of λ thus explain the observed fact that the two-dimensional gas pressure is negligible for palmitic acid films.

With a lower fatty acid such as butyric acid, however, the difference in energy between an isolated molecule in the surface and one located at the edge of a film is only 18 units so that it is not surprising that with these lower fatty acids the molecules, at least in dilute solutions, do follow the laws of two-dimensional gases.

That isolated molecules of palmitic acid in a water surface cannot exist in appreciable numbers is thus proved by the data of Table III and by the experimental observation that for values of a greater than say 40 A^2, the spreading force is immeasurably small. Thus Adam's view that the expanded films consist of molecules which are largely isolated cannot be correct. What is then the proper explanation of the expanded films?

In the 1917 paper in discussing the arrangement of molecules in adsorbed films on the surfaces of fatty acid solutions it was concluded (page 1888) that in dilute solutions "the hydrocarbon chain lies spread out flat on the surface of the water, but as the concentration of the solution increases, the molecules become more closely packed and when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically." The transition between the two states was assumed to take place in the manner that was suggested (on page 1865) for the expanded film of oleic acid, viz., in the expanded film "the molecules are partly reclining on the surface, while in the second case (comparessed film) they are packed tightly side by side and are more or less erect upon the surface."

The area covered by a vertically placed palmitic acid molecule is about 20 A^2 while the same molecule lying flat on the surface should cover an area of about 108 A^2 (see Table II). Clearly then the expanded film occupying an area of at most 40 A^2 must consist of molecules which are only slightly inclined from the vertical. As a matter of fact there is no reason at all why the flexible hydrocarbon chains should orient themselves at any particular angle. They will be quite free to respond to thermal agitation and arrange themselves nearly in the same random manner as in a liquid hydrocarbon, the only restriction upon their motion being imposed by the condition that the *lower end* of each molecule must remain in contact with the underlying water. We can thus readily see why the expanded films are *always liquid* while the contracted or fully com-

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pressed films of vertically oriented molecules are frequently *solid*. Taking the volume of the hydrocarbon chain in the palmitic acid molecule as 450 A^3 (Table II) we see that the thickness of the hydrocarbon layer (in A units) will be $450 \div a$ where a is the area of the film per molecule (in A^2 units). Thus when $a = 20$ A^2 the thickness is 22.5 A while for an expanded film for which $a = 33$ A^2 the thickness is 13.6 A. Such an expanded film is represented diagrammatically by 16 in Fig. 1, the area per molecule corresponding to the inclination shown being about $a = 60$ A^2.

Consider an expanded film as covering a definite area of a water surface. If additional palmitic acid molecules are introduced into the film there is no change in the area of the free hydrocarbon surface. The energy of transfer of a molecule from any given location to an expanded film is thus the same as the energy of transfer of the molecule to an interface between hydrocarbon and water as illustrated by Case 7 in Table III and Fig. 1. According to the data of Table III the value of λ for a molecule of palmitic acid at the edge of a condensed film is -17 (Case 14) while for a molecule in an expanded film (Case 7) λ is -37. This would indicate that the expanded film should form in preference to the condensed film. However, the difference of 20 in the values of λ is not greater than the probable error so that the sign of the difference is somewhat uncertain. In considering the stability of expanded films we must take into account the applied compressive force and the effect of the forces acting between the heads of the molecules which are located in the interface between the hydrocarbon film and the water. To understand these relationships better let us analyze the problem as follows.

Let n molecules of a substance (which spreads on water) be present per unit area as an expanded film on the surface of water. The flexible hydrocarbon tails of the molecules are subject to little or no constraint except that due to the fact that they are attached to the heads which are constrained to remain in contact with the water. This constraint may well influence the degree to which the thermal energy of agitation of the hydrocarbon tails aids in spreading the film and may thus alter the relation between the total energy and the free energy which should be used in connection with the Boltzmann equation. But as a first approximation we may ignore such an effect of the thermal agitation, especially as we are willing to regard the surface energies γ_R, etc., as empirical quantities.

The expanded film may thus be looked upon as a layer of hydrocarbon liquid having at its upper surface a surface energy γ_R and having adsorbed in its interface with the water n active groups, or heads per unit area. Consider now that by means of a *two-dimensional piston* (for example a paper strip on the surface) the expanded film is allowed to cover only a part of the surface of the water. The spreading force F (in dynes per cm) exerted by the film is measured by the mechanical force applied to the piston. On one side of the piston is a surface of water which exerts a force γ_W tending to cause the film

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to expand and on the other side is the expanded film whose ***upper surface*** exerts a force γ_R while the ***lower surface*** exerts a force which we may represent by γ_L. Thus for equilibrium we have

$$\gamma_W - F = \gamma_R + \gamma_L. \tag{7}$$

If the molecules in the film did not have any active groups, the surface tension γ_L would be equal to the normal interfacial energy γ_{RW}. But the ***active groups in the interface*** because of their thermal agitation will tend to act like a two-dimensional gas. When these active groups or heads are far enough apart they will exert a force F_L following the gas law

$$F_L = nkT. \tag{8}$$

When the molecules are packed as closely as in the ordinary expanded film, we should, by the analogy with the b term in the van der Waals equation, write

$$F_L\,(a - a_0) = kT \tag{9}$$

where a_0 is the area per molecule for a highly compressed film.

Furthermore, the analogy with the equation of state for gases would suggest that when the film is compressed sufficiently, attractive forces between the active groups would come into play and that these might be largely responsible for the small spreading forces observed with some contracted films. In any case, however, we may place

$$\gamma_L = \gamma_{RW} - F_L \tag{10}$$

and thus from Equation 7 we get

$$F = \gamma_W - \gamma_R - \gamma_{RW} + F_L. \tag{11}$$

For very low compressive forces we may neglect the attractive forces between the heads and thus by combining Equations (11) and (9) we get

$$(F - F_0)(a - a_0) = kT \tag{12}$$

as our equation of state for expanded films. Here F_0 is used as an abbreviation for the three γ terms in (11) so that

$$F_0 = \gamma_W - \gamma_R - \gamma_{RW}. \tag{13}$$

Thus we see that we should not expect the simple gas low of Equation 6 to hold for expanded films, but such a low should hold only after constants F_0 and a_0 have been subtracted from the observed values of F and a.

Examination of the experimental data on expanded films in my 1917 paper, and in Adam's papers, shows that the agreement with Equation (12) is very satisfactory. For large compressive forces deviations occur which are of the kind that are to be expected as a result of attractive forces between the heads of the molecules.[1] For example, Adam's curve (in this 3rd paper) for a film

[1] A fuller analysis of the experimental data on expanded films will be made in connection with a paper which is being prepared for the 3rd *Colloid Symposium* to be held at the University of Minnesota in June, 1925. See 3rd *Colloid Symposium Monograph* (Chemical Catalog Co., 1925)

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of myristic acid on water at 32.5°C gives the equation

$$(F+13)(a-18) = kT$$

The value of a_0 is thus 18 A² while F_0 has the value -13 dynes per cm.

Let us compare this value of F_0 with that calculated by Equation (13). For water at 32.5° the free energy (surface tension) γ_W is 7.10 dynes per cm. The interfacial free surface energy γ_{RW} of octane is 50.4. Since the temperature coefficient is very low the total interfacial energy is about the same as the free energy. Our theory of the structure of the interface leads to the conclusion that the *total energy* is independent of the length of the hydrocarbon chain and since in this case the free energy and total energies are nearly the same the free energy will also be independent of the chain length. Thus for tetradecane (the hydrocarbon corresponding to myristic acid) we may put $\gamma_{RW} = 50.4$.

The free surface energy of octane at 32.5° is 20.4 and the total energy is 48.4. For tetradecane the theory indicates that the total energy will also be 48.4. The free surface energy is a linear function of temperature and becomes zero at the critical temperature. Taking the critical temperature of tetradecane as 680°K we can thus estimate that the free surface energy at 32.5°C should be 26.8.

These values for the γ's give $F_0 = +0.2$ for octane and $F_0 = -6.2$ dynes per cm for hexadecane. This latter value does not differ greatly from that calculated from Adam's data on the myristic acid films ($F_0 = -13$). The difference is not greater than should be expected because of the uncertain part played by thermal agitation in the spreading of surfaces.

According to Equation (12) with negative values of F_0, the expanded film should not expand indefinitely even if the compressive force F is made negligibly small. Placing $F = 0$ we see that the maximum area covered per molecule will be

$$a_M = a_0 - \frac{kT}{F_0}, \tag{14}$$

For the case we have considered where $a_0 = 18$ and $F_0 = -13$, we obtain $a_M = 18+32.3 = 50.3$ A² as the maximum area for an "expanded film" of myristic acid on water. This equation shows that the maximum area a_M depends principally upon F_0. By Equation (13) we see that F_0 is the difference between two relatively large quantities which are nearly equal. A very small percentage change in γ_R causes a relatively large change in F_0 and therefore in a_M. As a matter of fact Adam finds that a_M varies only moderately for different substances. As the length of the chain increases he finds a slight decrease in a_M and considers this a strong argument against the view that the molecules tend to lie flat if they have sufficient room to do so. We have seen, however, by our comparison of octane with tetradecane that γ_R and therefore $-F_0$ increase with the length of the chain, and therefore by Equation (14) a_M should actually increase as the chain is made shorter. The changes in a_M observed by Adam may be accounted for by very small percentage changes in γ.

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Another factor which may need to be taken into account is that the value of γ_R for the CH_3 groups at the ends of hydrocarbon chains (particularly noticeable in iso-compounds) is about 10 per cent lower than for the CH_2 groups constituting the central portions of the chains. Thus as a film becomes more expanded the value of γ_R increases, tending to make the equilibrium of such a film more stable. Of course an expanded film can be dealt with by equations of the type we are now considering only as long as the upper surface forms a continuous hydrocarbon surface. The area of such a film is thus limited to that given by the molecules when they lie flat in the surface.

This theory of "expanded films" requires that the molecules remain in contact while Adam concluded that in such films the "molecules become separated and move about independently on the surface" and that "there are spaces not covered by molecules.". Adam considered that the molecules of the film behaved as a two-dimensional gas while we conclude that it is only the heads of the molecules that behave in this way.

It is hoped that the illustrations given in this paper have helped to prove the usefulness of the conception of separate surface energies for each of the different parts of complex molecules. It is believed that this viewpoint is applicable to the study of nearly all the physical properties of organic compounds, particularly to the calculation of the vapor pressures, solubilities, viscosities, and surface tensions of liquids and their mixtures.

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FORCES NEAR THE SURFACES OF MOLECULES

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IN THE EARLY development of the kinetic theory, during the last century, it was usual to consider the molecules of gases as rigid spheres, which exerted no forces on one another except at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but also for the viscosity, heat conductivity, and diffusion of gases, and other phenomena involving the free paths of the molecules.

By considering also attractive forces which varied with some power of the distance between the centers of the molecules, van der Waals was able to account for the main features of the transition from the gaseous to the liquid state, and also explained in a satisfactory manner the departures from the ideal gas laws which are shown by all gases at high pressures.

As new properties of matter are brought into consideration, or as a deeper understanding of them is needed, it is necessary to postulate additional properties of the molecules, and to know more accurately the nature of the forces acting between them. For example, to deal with the properties of electrolytes it is necessary to consider electric charges on the molecules or ions. In 1912 Debye showed that the electrical properties of many dielectrics could be accounted for by assuming that the center of gravity of the electrons in a molecule did not concide with the center of gravity of the positive charges of the nuclei. Thus the molecule possessed what we call a dipole moment, which can be measured as the product of an electric charge by the distance through which it is displaced. It is found, for example, that a molecule of water possesses a dipole moment of 1.8×10^{-18} electrostatic units. A moment of this magnitude could be produced by having an electron at a distance of 0.37×10^{-8} cm from a proton. Since there are 10 electrons in a water molecule, it is only necessary that the center of gravity of these electrons shall lie at a distance of 0.037×10^{-8} cm from the center of gravity of the three nuclei in the molecule. Thus displacements of the electrons to distances minute compared with the diameter of the molecule can account for even the largest values of dipole moments that have been observed.

[EDITOR'S NOTE: This paper appears as Chapter Ten in the author's book, *Phenomena, Atoms and Molecules*, Philosophical Library, 1950.]

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H. B. Hardy (1) in 1912 and the writer (2) (3) in 1916 pointed out that the fields of force around many chemical molecules must be very unsymmetrical, and that this resulted in an orientation of the molecules at the surfaces of liquids and in adsorbed films on solids. It was also found that the shapes which the molecules could assume, and which were determined by their chemical structures, were of great importance in connection with such properties as surface tension.

Within recent years, particularly through the work of Debye and his students, a great deal of knowledge has been accumulated regarding the electrical forces in liquids and solutions which contain ions and dipoles. Particularly in the study of electrolytes has this work cleared up many of the most serious difficulties of earlier theories.

There is now no need of drawing distinctions between chemical and physical forces. The chemist recognizes that many of the forces with which he has been dealing are electrical in nature, for, after all, molecules are built up of electrons and positive nuclei, and their interactions must necessarily be electrical. However, the simple classical theory of electrical forces based on Coulomb's law is wholly insufficient to account for chemical properties. With charged particles obeying Coulomb's law only, the minimum of potential energy is obtained when the positive and negative particles coincide. There must be something corresponding to repulsive forces holding the particles apart.

Repulsive Forces between Molecules

In many of the later developments of the kinetic theory where the molecules were regarded as rigid spheres, the repulsive forces which must counteract the attractive forces were assumed to act only during collisions — that is, at the instant of contact of the spheres (4). No explanation was attempted of the internal forces within the molecule which could result in this repulsion between molecules.

In order to account for the compressibility of solids, Born and Landé (5) have assumed that the repulsive force between molecules (or ions) varies inversely as a power of the distance between the centers of the molecules. Thus in the case of halide salts of the alkalis, such as NaCl, KI, etc., they showed that the compressibility indicated that the repulsive force varied inversely as the tenth power of the distance, while the attractive force resulting from the charges on the ions varied inversely as the square, in accord with Coulomb's law. Born (6) also attempted to show that the inverse tenth power law for repulsion could be deduced by assuming that the electrons and the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. First, the method of mathematical expansion which was used is not legitimate when applied to distances as short as those between ions in salts; and, second, Born assumed

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that the cubical ions were all orientated so that their edges were parallel. This kind of orientation would be unstable under the forces assumed, for these forces would tend to orientate one cubical ion so that its corner would come opposite the face of another ion, and in this case the repulsive force would be replaced by an attractive force which would act in addition to the force between the ionic charges. Although such orientation of ions as Born assumes might conceivably exist in solid crystals from causes which he does not discuss, it is clear that it cannot be the cause of the repulsive forces, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility.

Debye (7) has developed a theory which seems to give a better picture of the repulsive forces. Assuming the electrons to move in orbits in accord with Bohr's theory, he finds that the electric field around a molecule is a pulsating or partly oscillating field increasing in amplitude very rapidly as the surface of the molecule is approached. Thus when an electron approaches a molecule it acquires, in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the nonuniformity of the electric field near an atom the resulting force will be one of repulsion.

On this theory the repulsive forces between molecules are due to the perturbations in the electron orbits in one molecule, caused by the motions of the electrons in their orbits in the neighboring molecules. The repulsive force thus does not originate from a molecule as a whole, but comes from the close approach of electrons in the two molecules. This would seem to indicate that we may profitably regard these forces as *surface forces*, and should express them as functions of the distances between the surfaces of the molecules rather than in terms of the distances between the centers. This conception affords a justification, to a large extent, of the theory which regarded molecules as rigid elastic spheres.

Even if we accept Debye's picture of the origin of repulsive forces, we see that it really only refers the cause back to the quantum theory, by which the stable orbits of the electrons in the molecule are determined. At present, however, problems of this kind are treated by wave mechanics instead of by a consideration of orbits of electrons. For a few simple cases, such as interactions between hydrogen molecules, Hund and London have been able to calculate the forces by means of wave mechanics. But it will probably be a long time before definite knowledge of repulsive forces can be obtained in this way for more complicated molecules.

The quantum theory teaches that each electron in an atom is characterized by four quantum numbers, which are integers. Not all quantum numbers are possible; there are, for example, certain conditions (selection rules) which they must satisfy. The normal atom or molecule, with which the chemist is

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concerned, is one in which the electrons are so arranged that the total energy is a minimum, subject to the quantum rules that must be fulfilled.

It seems that the factor of greatest importance to the chemist is that which is known as the Pauli principle, which states that no two electrons in an atom can have the same combination of four quantum numbers. It is this principle which underlies the Periodic Table of the elements, and in a similar manner determines the arrangement of electrons in a molecule. It is through the development of methods of this kind that our greatest hope lies in obtaining a better understanding of the nature of repulsive forces.

For most practical purposes it is best for the chemist to regard molecules of organic substances as having shapes suggested by chemical structural formulas, and as having surfaces which are rather rigid so that strong repulsive forces are called into play for only moderate deformations. For many purposes it is still useful to look upon the surfaces as completely rigid.

Attractive Forces between Molecules[1]

Whereas the quantum theory seems essential in an understanding of the repulsive forces, the classical laws, such as the Coulomb law, are largely sufficient for dealing with the attractive forces between molecules. For example, the Debye-Hückel theory of electrolytes (8) is based on the Coulomb law, the Poisson equation, and the Boltzmann equation — all laws of classical mechanics.

In discussing forces between molecules, Debye has classified molecules in three groups: "(1) ionic, (2) polar and (3) non-polar." The ionic type is represented by electrolytic ions, such as K^+, NO_3^-, etc., and gaseous ions. In these molecules the number of electrons is unequal to the number of positive charges of the nuclei of atoms, so that the molecule as a whole has an electric charge which is some multiple of e, the charge of an electron. The polar type is represented by molecules which have a dipole moment — that is, uncharged molecules in which the center of gravity of the negative charges does not coincide with that of the positive. Non-polar molecules thus include all molecules which are uncharged and in which the centers of gravity of the positive and negative particles coincide. From Debye's point of view such molecules may correspond to quadrupoles, octopoles, etc. For example, positive and negative charges arranged alternatively at the corners of a square will give a quadrupole, at the corners of a cube an octopole. In forming clear conceptions of the attractive forces between molecules it is useful to consider the actual magnitude of the forces involved.

Ions

The electric field at a distance r from a univalent ion having a charge e is $e/\varepsilon r^2$, where ε is the dielectric constant of the medium. The charge of the electron, e, is equivalent to 1.43×10^{-7} volt centimeter and thus the electric

[1] The term "molecule" is to be used in its broad sense, which includes atoms and ions.

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field is $1.43 \times 10^{-7}/\varepsilon r^2$ volts per centimeter, and the electric potential corresponding to this force is $1.43 \times 10^{-7}/\varepsilon r$. If we take for r the value 3×10^{-8} cm, which corresponds roughly to the distance between two ions in contact, we find the electric field to be 1.6×10^{8} volts per centimeter and the potential to be 4.8 volts. Taking for ε the value 80, corresponding to the dielectric constant of water, we would obtain values only one-eightieth of those given. However, it is doubful if the conception of dielectric constant is entirely justified at distances as short as this for we can hardly speak of two molecules in contact as being in a medium having known electrical properties. At distances several times greater than the molecular diameter the use of dielectric constant in this way is justified.

The applications of the Debye-Hückel theory to electrolytes prove that the forces at these larger distances are of vital importance in an understanding of the properties of ions. According to the Coulomb law the force between two ions varies inversely as the square of the distance. In electrolytic solutions the increased concentration of positive ions around negative ions, and *vice versa*, causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law.

Polar Molecules

At a distance r from a dipole molecule having an electric moment μ the electric potential is $\mu \cos \theta/r^2$, where θ is the angle between the radius vector r and the axis of the dipole. It can thus be found that at a distance r along the dipole axis the electric field is $-2\mu/r^3$, this force being in a direction of the polar axis. At a distance r in the equatorial plane of the dipole the electric force is also in a direction parallel to the polar axis but has the magnitude $+\mu/r^3$.

Debye (9) has shown that in general because of thermal agitation a dipole (or quadrupole) molecule in a gas or liquid is changing its orientation so fast that we must not regard the force produced by a dipole as a steady force, but a rapidly fluctuating force, and under these conditions many of the effects produced by the force are proportional to $\bar{E}^2$ or the mean square field. The effective force can thus vary inversely as the sixth power of the distance from the dipole.

Non-polar Molecules

If the molecule is a quadrupole the instantaneous force in any given direction will vary inversely as the fourth power of the distance, and thus the effective fluctuating force will vary inversely as the eighth power of the distance. With more symmetrical molecules the forces will vary inversely with still higher powers of the distance.

Under the influence of forces of the kinds we have been considering the various types of molecules in liquids respond in different ways. Positive ions tend to concentrate around negative ions in the manner considered by the Debye-Hückel theory (8). Dipole molecules tend to be orientated by the

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field in the neighborhood of the ion. Thermal agitation tends to prevent this orientation, so that only when the dipole molecule is very close to the ion is the orientation of the molecule complete.

The dipole molecule, orientated in a field, tends to move in the direction towards which the field is of greater intensity. The change in potential energy is mE, where E represents the change in field strength and m is the effective dipole moment (average moment) in the direction of the field.

A field insufficient to orientate the dipoles completely gives an effective dipole moment m, which according to Debye (10) is

$$m = \mu^2 F/3kT$$

where F is the electric force tending to produce the orientation. Since the energy available for producing motion of translation in a dipole is proportional to mF, we see that at large distances dipoles attract one another in proportion to F^2 and therefore in inverse proportion to the sixth power of the distance. If, however, we consider a fixed dipole (for example one attached to a large organic molecule) acting on another dipole at a very short distance so that the latter is orientated by the field of the former, then the force of attraction will vary inversely as the fourth power of the distance.

An electric field of intensity F, acting on a non-polar molecule, causes a deformation, or polarization, of the molecule so that it acquires a dipole moment m given by

$$m = \alpha F$$

where α is the polarizability. A liquid made up of non-polar molecules of this kind will have a dielectric constant ϵ which is greater than unity, and the *molar polarization* of the liquid is calculated from ϵ by means of the equation

$$P = \left(\frac{\epsilon-1}{\epsilon+2}\right)\frac{M}{\varrho}$$

where M is the molecular weight and α is the density of the liquid. The relation between P and α is given by the equation

$$P = \frac{4\pi}{3} N\alpha = 2.54\times 10^{24}\alpha$$

where N is the Avogadro number, 6.06×10^{23}. The quantity P has the dimensions of a volume and is thus measured in cubic centimeters. For ordinary organic liquids the value of P is roughly about 0.3 of the volume of a gram-molecule. A few values of P and α are given in Table 1. From the value $\alpha = 10^{-23}$, which is of the order of magnitude found in most organic liquids, we can calculate that the electric field needed to give to a non-polar molecule a dipole moment of 10^{-18} is $F = 3.0\times 10^7$ volts per centimeter. This is the field that would exist at a distance $r = 7\times 10^{-8}/\sqrt{\epsilon}$ cm from an electron. A field of

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magnitude would be found at the distance $r = 2.7 \times 10^{-8}/(\epsilon^2)$ in the direction along the axis of the dipole.

From the foregoing discussion, we see that the effects of the electric fields of molecules are of three kinds which we may classify as (1) segregation, (2) orientation, and (3) deformation. As an example of segregation, we have the segregation of positive ions around negative ions in electrolytes. Dipole molecules become orientated in the field produced by any other molecule and thus

TABLE I

Values of P and a

	P	*a*
	cc.	
H_2	5.8	2.28×10^{-24}
N_2	13.6	5.4
CH_4	21.0	8.3
C_6H_6	25.8	10.2

are attracted toward the molecule producing the field. Non-polar molecules, under the influence of fields of other molecules, become deformed or polarized so that they acquire a dipole moment in the direction of the field and are thus attracted by the molecule producing the field.

In estimating quantitatively the magnitude of the segregation and orientation that result from molecular fields, we may apply the Boltzmann equation;

$$\frac{n_1}{n_2} = A\,\varepsilon^{\lambda/kT}$$

where n_1 and n_2 represent the relative numbers of molecules in two given positions, or orientations, and λ is the work done in transferring a molecule from one of these states to another. The constant A involves the ratio of the *a priori* probabilities of the molecules in the two regions or states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. The quantity ε in this equation is the base of the natural system of logarithms, 2.718; k is the Boltzmann constant, 1.37×10^{-16} erg per degree; T is the absolute temperature.

We see from the Boltzmann equation, that when the constant A is not too far removed from unity, the effects of segregation and orientation usually begin to be important only when the energy λ becomes of the same order of magnitude as kT. At room temperature the value of kT is 4.1×10^{-4} erg, which is the energy that an electron would acquire in falling through a potential of 0.025 volt.

In Debye's theory for the contribution of dipole molecules to the dielectric constant of liquids, it is shown that the effective dipole moment m of the dipole

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molecules (of moment μ) is $\frac{1}{2}\mu$ when the field is of such intensity that the work done by the field in orientating the molecule is equal to $2kT$.

The segregation of ions of one sign around an ion of the opposite sign will be marked at distances r less than that at which the potential is 0.025 volt; that is, when r is less than $57\times10^{-8}/\varepsilon$ cm. If ε has a low value, of a few units only, then even in very dilute solutions, where the distances between the ions are more than ten times greater than the molecular diameters, the ions will tend to be swept out of the solution and brought into contact with each other. This is in accord with the fact that such salt-like substances as NaCl, whose crystals are held together by forces of the Coulomb type, are practically insoluble in organic liquids of low dielectric constant. On the other hand, in water and other liquids of high dielectric constant, in solutions of even moderate concentration, the ions are far enough apart so that their potentials with respect to one another are less than kT, which agrees with the fact that these salts are soluble in these liquids, and that their solutions behave as electrolytes.

We have seen that to orientate the larger portion of dipole molecules in liquids requires a field F which makes μF greater than $2\,kT$. This means that a field of about 2.4×10^{7} volts per centimeter is needed for the orientation. The work done when the orientated molecule is brought into the field is of the same order of magnitude, so that a field sufficient to cause nearly complete orientation of dipole molecules will also cause marked segregation. A field of 2.4×10^{7} will exist at a distance $r = 8\times10^{-8}/(\varepsilon)^{\frac{1}{2}}$ cm from a univalent ion, or at a distance $r = 3\times10^{-8}/(\varepsilon)^{\frac{1}{2}}$ cm along the axis of a dipole molecule having a moment $\mu = 10^{-18}$. In other directions than along the dipole axis the force will be less and therefore the distance at which effective orientation or segregation occurs will be less than that just given.

From these calculations we conclude that the interaction between dipole molecules of moment 10^{-18} can cause mutual orientation only when they are practically in contact. If they were separated by one additional molecule, so that the distance between centers is 6×10^{-8} cm, even if they were still orientated, the force would be only one-sixteenth as great, since it varies inversely as the fourth power of the distance. However, at this greater distance, the orientation would be far from complete, so that the force would actually vary inversely as the sixth power of r, and would thus be only one sixty-fourth as if the molecules were in contact.

The electric force necessary to deform a molecule sufficiently to give it a dipole moment $\mu = 10^{-18}$ (viz., 3×10^{7} volts per centimeter) is practically the same as that needed to produce orientation of a dipole molecule having this same moment. Thus when two dipole moment molecules are in contact, the dipole moment which each possesses is practically doubled because of their mutual deformation.

Taking the electric field near a dipole to be proportional to r^{-3}, and remembering that the distance between the center of one molecule and the sur-

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face of its neighbor is only one-third the distance to the surface of the far neighbor, we realize that the electric field intensity at one side of the dipole molecule is twenty-seven times as great as at the opposite side.

The latent heat of evaporation of a liquid expressed per molecule gives the energy which must be expended to separate the molecules of liquid from one another. Pentane, a non-polar liquid, which boils in the neighborhood of room temperature (36°C), has a heat of evaporation of about 40×10^{-14} erg per molecule, which is roughly equal to $10\,kT$. According to the rough empirical rule of Trouton, the absolute boiling points of liquids are proportional to their latent heats of evaporation, so that in general, to the same degree of approximation, the heats of evaporation per molecule for all liquids will be about $10\,kT$, where T is the temperature at the boiling point. This can be looked upon as a consequence of the Boltzmann law. The coefficient A in this case, however, is quite different from unity.

The energy involved in the close approach of ions to within molecular dimensions is far greater than $10\,kT$ — at least when the medium is one of low dielectric constant. Thus we are not surprised at the fact that substances built up of ions are solid bodies which melt and boil only at very high temperatures, and are soluble only in liquids of high dielectric constant.

We have found that the energies involved in the approach of dipole and non-polar molecules (having values for μ of about 10^{-18}, and for α of 10^{-23}) to within a distance of 3×10^{-8} cm is approximately equal to kT ($T = 300°\text{K}$). Since a given molecule will usually be in contact with about a dozen others, it is to be expected that the energy necessary to separate a molecule from all its neighbors would be of the order of magnitude of $10\,kT$. In fact, we can reasonably expect values larger than this because of the fact that the greatest effects will be produced in the deformation of the molecule on its side facing the adjacent molecule ($r = \frac{1}{2}$ molecular diameter), the electric field there being about eight times greater than at the center of the molecule.

We thus have an explanation of the fact that liquids whose molecules have the properties we have postulated will, in general, have boiling points considerably above room temperature. When the molecules are in contact the energies of the non-polar molecules are not very greatly different from those of the dipole molecules — at least are of the same order of magnitude. In this we have an explanation of the fact that the boiling points of liquids containing dipole molecules are only moderately higher than those of non-polar substances. It is possible, for example, to have liquids whose molecules are dipoles, such as anhydrous hydrogen chloride, which boil at temperatures far below room temperature.

Our analysis of the known electrical forces causing the interactions of molecules thus leads us inevitably to the conclusion that the forces involved in holding together the molecules of organic liquids are acting almost wholly between molecules *in contact*, and that in general no serious error would be

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made in neglecting all forces which act at greater distances. This conclusion is, I believe, thoroughly justified in the case of all liquids built up of non-polar molecules. It applies with reasonable accuracy to most liquids having molecules containing dipoles. But in general, where liquids contain free ions the range of the forces is much greater, and we must then take into account the Coulomb forces which act at greater distances.

For many years, in connection with studies of adsorption, surface tension, and the kinetics of heterogeneous reactions, the writer has found it extremely useful to explain these phenomena in terms of actions between molecules *in contact*. From an empirical point of view the results have justified this method of attack. In many ways this conception is in accord with chemical tradition, for the chemist has always considered that chemical action between molecules takes place between molecules in contact.

The physicist, probably ever since the time of Newton, has been rather inclined to consider forces which vary as some power of the distance, or to deal with fields of force which extend throughout space. The remarkable success of the physicist in the development of the atomic theory, and more recently, in some of the applications to chemical phenomena, such as those involved in the properties of electrolytes, seems to have made many chemists and physicists believe that these methods would also provide the solutions to more complicated chemical problems.

It must be emphasized, however, that the physicist, in attempting to calculate the manner in which dipole molecules or non-polar molecules will interact in liquids, meets problems which are mathematically so complicated that it is necessary to make simplifying assumptions. For example, the potential energy of dipole or non-polar molecules with respect to one another is expressed as an infinite series in which the successive terms involve as factors $1/r$, $1/r^2$, $1/r^3$, etc. The coefficient of the first term for the case of dipole molecules is 0, the coefficient of the second term is then calculated with great care and often with great difficulty; and although the coefficients of the third and subsequent terms are known not to be zero, these terms are neglected because of the fact that they involve higher powers of r. We have seen, however, that the forces which are primarily important in liquids are those between molecules in contact, and that a small increase in the distance causes the forces to become very small. For example, with a force varying with $1/r^9$, such as Debye finds with non-polar molecules, the energy involved in the approach of two molecules would fall to one-half value if the distance between the molecules were increased 15 per cent. This change in energy has its effect in the exponent of the Boltzmann equation, so that most of the actions of importance must occur with only still smaller variations in the distance r. It is obvious, therefore, that even for the roughest kind of approximation one is not justified in neglecting the term involving $1/r^3$ in comparison with that which involves $1/r^2$.

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As another example of the kinds of approximation that are necessary in treating mathematically the forces between dipole molecules, we have Debye's treatment of the relations between dielectric constant and chemical association (11). He considers the effect of dipoles on one another as the concentration of the dipolar molecule increases in a non-polar solvent. Assuming the molecules to be spheres, complicated equations are derived allowing for the interactions. The result is that the dipole moment per molecule increases with concentration because the molecules tend to line up along a common axis. This is due to the fact that the force along the polar axis is twice as great as in the equatorial plane for a given value of r. An analysis of experimental data, however, shows that in solutions of many dipole substances in non-polar solvents, the polarization per molecule decreases as the concentration increases. Such a result could be explained if the molecule instead of being a sphere were ellipsoidal with the equatorial diameter less than 80 per cent of the polar diameter. The introduction of such a concept would introduce far too great mathematical complications to make an analysis worth while.

Perhaps the greatest objection to a mathematical treatment of the properties of liquids in terms of power laws of force is that it becomes practically impossible to take into account the effects resulting from the complicated shapes of molecules which must characterize organic substances, according to the structual formulas of the chemist. If now we assume that the forces between molecules come into play only at their areas of contact, we have simplified the problem mathematically to such an extent that we can take into account our knowledge regarding the shapes of the molecules which can be furnished us by the chemist. Of course, in so doing we are making approximations, but the errors so introduced will, I believe, usually be far less than those which are often made by the physicist in dealing with these problems. I should like to outline now the ways in which a conception of surface forces can be developed to give concrete pictures and quantitative results for many problems which are too difficult to handle by the method involving the power laws of force.

In considering that the interactions between molecules occur at their surfaces of contact, it is not necessary to assume that the nature of the forces at any given part of the surface is characteristic wholly of the atom underlying the surface. The chemist knows, for example, that the properties of an organic molecule are not simply the sum of the effects due to the separate atoms in the molecule. If one of the hydrogen atoms in the methyl group of acetic acid be replaced by a chlorine atom, the effect of the greater charge on the kernel of the chlorine atom as compared with that of the hydrogen atom which it replaces, is to displace the electrons in the carboxyl group in the direction towards the chlorine atom. This displacement of the pair of electrons which hold the nucleus of the hydrogen atom of the carboxyl group causes the hydrogen nucleus to be held less firmly, and thus makes it easier for the hydro-

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gen nucleus to pass over to a water molecule (in aqueous solutions of acetic acid) to form an OH_3^+ ion, which is the so-called hydrogen ion characteristic of acids. We thus have a clear indication of an alteration in surface forces which may extend over the whole surface of the molecule as a result of the replacement of a hydrogen atom by a chlorine atom.

We may form a clearer conception as to the magnitude of these changes in the surface forces due to effects transmitted from atom to atom in the molecule, by considering the chlorine-substituted fatty acids. In Table 2 the values of the dissociation constant K for some of these acids are given as taken from Landolt-Börnstein tables. In the third column, under the heading ln r, is

TABLE II

Dissociation Constants of Chlorine-substituted Fatty Acids

	K	ln r	volts
Acetic acid	1.85×10^{-5}	[0]	0
Chloroacetic	155.0	+4.44	0.1053
Dichloroacetic	5000.0	7.6	0.190
Trichloroacetic	20,000.0	9.3	0.233
Propionic acid	1.4×10^{-5}	[−0.26]	−0.006
α-Chloropropionic	147.0	4.36	0.1045
β-Chloropropionic	8.6	1.53	0.0382
Butyric acid	1.5×10^{-5}	[0.21]	−0.0053
α-Chlorobutyric	139.0	4.30	0.1038
β-Chlorobutyric	8.9	1.57	0.0392
γ-Chlorobutyric	3.0	0.48	0.012

given the natural logarithm of the ratio of K for the acid in question to the value of K for normal acetic acid. According to the Boltzmann equation, this quantity should be equal to λ/kT, where λ represents the difference between the work necessary to remove a hydrogen ion from the given acid molecule and from an acetic acid molecule. Since kT is equivalent to 0.025 volt, we can obtain the value of λ in volts by multiplying the values of ln r by 0.025; the last column of the table gives these values.

Comparing the monochloro acids with each other, we see that all three of the acids in which the chlorine is in the α-position give $\lambda = 0.105$ volt. The two acids with chlorine in the β-position give $\lambda = 0.039$ volt. The single γ-chloro acid for which data are available gives $\lambda = 0.012$ volt.

From theoretical considerations we should expect that any state of strain which is transmitted from atom to atom along a hydrocarbon chain should decrease exponentially as the distance increases. The above data thus leads to the conclusion that the electric polarization produced by the presence of a chlorine atom in a hydrocarbon chain decreases in the ratio 2.7: 1 in being

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transmitted from one carbon atom to the next. If instead of chlorine we should substitute other radicals, we might obtain electric forces of different magnitudes, but in any case we should expect this ratio 2.7:1 to apply to the decrease in the force from atom to atom. A considerable effect is thus transmitted from one atom to the next, but very little is transmitted as far as the second or third atom.

This result justifies us in attributing definite properties to different parts of the surface of the molecules of aliphatic compounds. For example, the field of force around a carboxyl group in a fatty acid should be independent of the length of the hydrocarbon chain, provided that this is more than about two carbon atoms long. That is, the forces near the surface of the carboxyl group should be practically constant for all the acids higher than propionic acid and would be roughly the same in the case of acetic acid, but might be considerably different in the case of formic acid. Similarly, we should not be able with any reasonable accuracy to regard the field of force around the carboxyl group as due merely to the super-position of the effects of the hydroxyl group and the carbonyl group, for these two groups are too close together in the molecule to be without important effect on one another.

Principle of Independent Surface Action

From the foregoing analysis of the forces acting between molecules of various types, we conclude that there is a large class of substances for which we are justified in regarding the forces between two molecules in contact as being dependent mainly on the nature of the surfaces of the molecules which are in contact. This principle of independent surface action (12) will always be only an approximation to the truth, but there are many cases where it applies with sufficient accuracy and so greatly simplifies the problems of the interactions between molecules that useful results are obtained in problems so complex that no solution is otherwise possible. Let us consider some of these problems.

The theory of adsorption in monomolecular films on solids and liquids (13) is an example of the application of this principle. According to this theory, the force which holds an adsorbed molecule or atom on a surface depends on the character of the surface of contact between the molecule and the solid. If a second layer of molecules should form, the forces holding the molecule to the second layer are thus entirely different from those holding the molecules of the first layer. The rates of evaporation of the molecules from the first layer or from the second layer will differ greatly, especially since they depend upon the magnitude of the forces according to an exponential relation of the Boltzmann type. Two general cases must be considered. If the forces holding the molecules in the first layer are greater than those holding those of the second, there will be a wide range of pressures of the adsorbed gas for which the film will never exceed one molecule in thickness. We thus arrive at the

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conception that a certain fraction, θ, of the surface is covered by adsorbed molecules, and that the properties of this adsorbed film depend primarily on θ. If the forces between these molecules and the underlying surface are very large compared to those that act between adjacent molecules, then, for example, we may conclude that the rate of evaporation of the adsorbed molecules will be proportional to θ. This simple conception leads to an adsorption isotherm which has been found to hold experimentally in a large number of cases. However, if the forces that act between adjacent adsorbed molecules are not negligible, there will be large deviations from this simple law, but the theory may be easily extended to take into account such forces. The forces may be those of attraction, or, if the molecules become dipoles as a result of the adsorption, or if they become crowded, their interaction may cause repulsive forces.

The second important case (14) to be considered is that in which the forces that hold the second layer of molecules are greater than those which hold the first; or, more generally, the case in which the forces acting between adjacent adsorbed molecules are greater than those with which each of these is held on the underlying surface. There is then great difficulty in getting any appreciable number of molecules in the first adsorbed layer, and single molecules or atoms or groups of molecules in the first layer act as nuclei from which large aggregates or crystals may develop. The condensation of cadmium or mercury vapor on cooled glass surfaces is an example of this type. It is possible to formulate the problem quantitatively and to express the number of nuclei that will form per second as a function of temperature and pressure. The calculated values are in good agreement with those obtained by experiment. If definite numbers of isolated copper atoms are evaporated on to a clean surface, each one serves as a nucleus for the formation of cadmium crystals, when the temperature of the surface and the pressure of the cadmium vapor are carefully regulated, and thus by dark field illumination of the surface the copper atoms can be directly counted. Some experiments made several years ago by Mr. Harold Mott-Smith have shown that this method can be developed to count atoms just as the C. T. R. Wilson method can be used to count ions.

In case the adsorbed atoms on a metallic surface are electrically charged or acquire large dipole moments, electrical forces are brought into play which may make the principle of independent action inapplicable. For example, the rate of evaporation of electrons from a tungsten surface at high temperature is enormously increased by the presence of adsorbed thorium (15) or caesium (16) atoms on the surface. But the increase in the number of electrons which evaporate is not even approximately proportional to the amount of thorium or caesium which is present on the surface. The same is true for the evaporation of positive caesium ions from a tungsten surface. In both of these cases, the heat of evaporation of electrons or ions varies approximately linearly

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with θ, the fraction of the surface covered by the adsorbed atoms, and thus, according to the Boltzmann equation, the logarithm of the rate of evaporation of electrons or ions varies linearly with θ. In the case of the evaporation of neutral atoms — for example, atoms of oxygen from adsorbed films on heated tungsten filaments — the rate of evaporation is much more nearly proportional to θ.

In studies of the surface tensions of organic liquids (2) (17) and of the properties of adsorbed films of organic substances on water (3) (4) and of oil films on water, the principle of independent action has proved itself particularly useful. It gives immediately a simple reason for believing that these films should rarely be more than one molecule in thickness; or rather, that if they are more than one molecule in thickness, their properties will be markedly different from those of films in which the surface is not completely covered with a single layer. The theory also gives immediately reasons for believing that adsorbed films of many organic substances on water will consist of orientated molecules. Thus the area on a water surface occupied by molecules of the various fatty acids is dependent on an interaction between the carboxyl group and the water, and is independent of the length of the hydrocarbon chain. This simple result, proved by experiment, demonstrates that the molecules are orientated so that the carboxyl group is in contact with the water, leaving the hydrocarbon tails to form a layer above the carboxyl group which will have the properties characteristic of a liquid hydrocarbon.

The theory is equally applicable in pure organic liquids. The total surface energies (surface tension extrapolated to the absolute zero) of hexane and of hexyl alcohol are practically identical. This is readily explained by the orientation of the molecules which prevents the hydroxyl groups from coming in contact with the surface, so that in both cases the actual surface is that of a pure hydrocarbon.

Studies of the surface tension of aqueous solutions of various aliphatic compounds in water prove that in concentrated solutions the surface becomes covered with a closely packed monomolecular film consisting of orientated molecules like those in oil films. With sufficiently dilute solutions, however, the amount of substance adsorbed in the surface is not enough to cover the whole surface with closely packed molecules. Under these conditions, the hydrocarbon chain lies flat in the water surface and the energy needed to transfer any molecule from the surface to the interior increases by a definite amount for each additional CH_2 group in the hydrocarbon chain. This is an excellent example of the application of the principle of independent surface action, each CH_2 group producing its effect independently of the others.

Similar views prove useful in studies of many other properties of matter. Consider, for example, jellies made by amounts of gelatin or soaps in concentrations less than 1 per cent by weight. The elasticity proves the existence of a continuous frame-work of molecules in contact, extending throughout the liquid. The time of relaxation of such jellies serves as a measure of the rate

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at which the molecules which form the chains separate or evaporate from one another. Guided by these views, I made some experiments, over ten years ago, to determine the diameters of the cross sections of the fibers or rods that must be the elements of the rigid frame-work. For this purpose I made up some dilute gelatin jellies on filter pager and measured the rate at which water could be forced through the jellies by applying a definite pressure. By a modification of Stokes' law which gives the rate of fall of small spheres in liquids, it was possible to calculate the force necessary to move small cylinders of various diameters through a liquid. This law was then checked experimentally by measuring the rate at which water passed through a column of glass-wool having fibers of known size. Applying this law to the case of the motion of water through a gelatin jelly, it was thus possible to calculate the size of the fibers. Only rough experiments were made, but the results showed clearly that the diameter of the fibers was approximately 10^{-7} cm.

I believe that there is real justification for dealing with molecules of this character, at least as a first approximation, as though they followed the same laws as bodies of large size, such as the fibers of glass-wool. Einstein showed, years ago, that Stokes' law could be used, approximately, for the study of the rate of migration of ions through water solutions. I believe that a thorough quantitative study of the forces necessary to drive water through various jellies should give much valuable information as to the structure of these jellies.

Very useful pictures of the mechanism involved in the viscosity of liquids and of diffusion in liquids and solids may be had by considering that molecules in contact exist in two states: one in which the surfaces are rigidly connected, the other in which they are entirely free to move. The behavior of the molecules is thus analogous to that of a gas condensing on a solid; the molecules of the gas strike the surface, remain adsorbed for a certain time, and then evaporate off again. Applying this conception to molecules in liquids, we see that the motion of the molecules past each other, involving viscosity and diffusion, depends upon the relative times during which the molecules are in this rigid, or in this mobile contact. These times can be calculated from an equation of the Boltzmann type in terms of the energy difference between the two states. This theory accounts for the frequent occurrence of temperature coefficients of viscosity and diffusion, which agree with the Boltzmann equation. It seems also to account for the fact that the viscosity of different members of a series of hydrocarbons increases in geometrical proportion to the length of the chain. It would seem that the principle of independent surface action should afford a means for the development of a simple theory of viscosity which would take fully into account the shapes and sizes of the molecules and of the different chemical groups contained in the molecules.

The principle has also found many applications in connection with the mechanism of heterogeneous chemical reactions. The interaction of oxygen and hydrogen and of carbon monoxide and oxygen at low pressures in contact

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with a heated platinum filament (18) has shown that equations which are based directly on this principle are in excellent agreement with the experimental results over very wide ranges of pressure and temperature. For example, the experiments showed that at low temperatures the reaction velocity was accurately proportional to the partial pressure of oxygen and inversely proportional to the pressure of carbon monoxide. This behavior could be completely accounted for by assuming that the rate of reaction was determined by the rate at which oxygen molecules could reach holes in the films of adsorbed carbon monoxide which were left by evaporation of carbon monoxide molecules, or which were formed by the removal of the carbon monoxide by the oxygen which reached these holes. The poisoning effect of the carbon monoxide was due to the fact that the opportunity for the oxygen to reach the holes was decreased if the carbon monoxide molecules were able to fill up the holes before the oxygen arrived. It seems difficult to reach quantitative agreement with these experiments except by the application of the principle of independent surface action.

The interaction of hydrogen and oxygen in contact with tungsten filaments at temperatures ranging from 1500° to 2500°K is another illustration of a similar kind. Oxygen acts to form WO_3 at a rate proportional to the oxygen pressure (19). Oxygen atoms *in the adsorbed oxygen film* do not react with one another and with the tungsten to form WO_3 even at the highest temperatures. At 1500°K the life of oxygen atoms on the surface is of the order of years; at 1860°K it is about 25 minutes; and at 2070°K it is 15 seconds. When the atoms leave the films at the higher temperatures they do so as free atoms, not as molecules. Thus, even in the presence of minute pressures of oxygen, the tungsten surface is practically completely covered with a single layer of oxygen atoms. Oxygen molecules which strike this surface condense on it, but evaporate from this second layer at a relatively high rate; but while thus adsorbed, they move freely over the surface and are able to fill up any holes that form in the first layer. Also the molecules, while adsorbed in the second layer, have a certain probability of interacting with those of the first layer and with the underlying tungsten to form WO_3, and the holes thus formed by the removal of oxygen from the first layer are soon filled up by the migration of the molecules of the second layer.

Hydrogen molecules are not able at any temperature to react directly with the oxygen in either of the first or second layers (10), but if they reach the tungsten at one of the holes in the first layer, they react immediately with the adjacent oxygen. Thus when the oxygen pressure falls to a certain low critical value, the hydrogen completely removes all the oxygen from the surface, and it does this suddenly. The hydrogen which then strikes the film is dissociated into atoms to an extent that depends upon the temperature, and the atomic hydrogen formed goes to the bulb and reacts with the WO_3 which has previously been deposited there.

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This theory which can readily be stated quantitatively appears to be in complete agreement with all the experimental facts, so that again we find support for the principle of independent surface action.

The molecules in adsorbed films on solutions of organic substances in water are frequently in a state of a two-dimensional gas. Oil films on water may exist as solid or liquid films. In the case of so-called expanded films (12), the heads of the molecules act as a two-dimensional gas, while the tails form a two-dimensional liquid. The molecules of oils adsorbed on solids, such as those that are responsible for some of the lubricating properties of oils, and those involved in the phenomena of flotation of ores, usually show little or no tendency to move over the surface. In other words, the molecules appear to be attached rigidly to the surface.

Many of the equations that were developed in the quantitative studies of the velocities of heterogeneous reactions assumed that bare spots on the surfaces were distributed over the surface according to statistical laws. Such statistical distribution would not occur unless the molecules possessed a certain degree of mobility over the surface, for the molecules that are removed by the reaction are those that are adjacent to holes already existing. Volmer and others have shown experimentally that adsorbed atoms frequently possess great mobility even on solid surfaces and thus act like two-dimensional gases of high viscosity.

I believe that the principle of independent surface action will be useful in studying many properties of organic substances which have hitherto been too complicated to be treated quantitatively. Within recent years I have made some attempts of this kind.

When a liquid is separated into two parts, along a surface having an area of 1 sq. cm, two new surfaces with a total area of 2 sq. cm are formed. The surface tension or free surface energy measures the work done per unit area in forming the new surfaces. The total surface energy γ, which is equal to the free surface energy extrapolated back to the absolute zero, represents the total energy change per unit area. For all the pure hydrocarbons, such as pentane and nonane, γ is equal to about 48 ergs cm^{-2}. The fact that this value is practically independent of the length of the hydrocarbon chain proves that the surface forces are very nearly uniform over the whole of the hydrocarbon molecule.

When a hydrocarbon, such as hexane, evaporates, molecules pass from the interior of the liquid into the vapor. If we consider a drop of hexane liquid to be removed from a large volume of the liquid into the free space above it, the work that would be needed to form this drop would be equal to $S\gamma$ where S is the surface area of the drop. Since we are regarding molecules as having surfaces possessing certain properties, we may say that the work necessary to remove a single molecule of hexane from the liquid, which is the latent heat of evaporation per molecule, will also be equal to $S\gamma$, where S is now the

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surface area of the molecule and γ is the surface energy of the molecule per unit area.

The molecular surface S for the molecule of vapor may be calculated from the molecular volumes (molecular weight divided by density), assuming the surfaces to be the same as in the case of closely packed spheres. This assumption would probably be quite accurate for large molecules, but would be only a rough approximation in the short chain hydrocarbons. From the known values of the latent heats of evaporation, the values of γ can then be calculated. Practically all of the normal hydrocarbons, with the exception of methane, give the value $\gamma = 34 \pm 1$ ergs cm^{-2}. This value is of the same order of magnitude as the value 48 found from measurements of surface tension. The fact that γ is found to be constant proves that the work done in removing molecules from the liquid to the vapor phase is strictly proportional to the molecular surface. In other words, the latent heat of evaporation is proportional to the two-thirds power of the molecular volume.

This theory can readily be extended to cover the case of the heats of evaporation of the various aliphatic alcohols. If S is the total surface of the molecule of vapor, then aS is the surface of the head of the molecule (hydroxyl group) while cS is the area of the tail (hydrocarbon chain). We may let γ_a and γ_c represent the surface energies per unit area of the heads and tails respectively when the molecule is in the vapor phase. Thus $Sa\gamma_a$ is the total energy of the head and $Sc\gamma_c$ the total energy of the tail.

If the molecules of alcohol in the liquid phase were arranged at random, that is, if they did not orientate each other appreciably, and did not tend to form clusters (segregation), then it may readily be shown that the total interfacial surface energy in the liquid between the hydroxyl groups and the hydrocarbon chains will be $Sac\gamma_{ac}$, where γ_{ac} is the interfacial surface energy per unit area. We should therefore be able to calculate the latent heat of evaporation, λ, from the difference between the energies in the vapor and liquid phases.

$$\lambda = S(a\gamma_a - ac\gamma_{ac} + c\gamma_c)$$

If we take $\gamma_a = 193$, $\gamma_c = 34$, and $\gamma_{ac} = 34$, we get excellent agreement between the observed latent heats of evaporation and the structures of most monobasic alcohols. We have already seen that γ_c is equal to 34 as the value found for the evaporation of pure hydrocarbons. The value $\gamma_{ac} = 34$ was found as a result of experiments on the vapor pressures of mixtures of alcohol and water. The interfacial energy between water and a hydrocarbon is about 59, so that the value 34 is of the right order of magnitude. The surface energy of water is 117, but this naturally represents the surface energy of the least active part of the water molecule, whereas the energy γ_a equal to 193 corresponds to the most active part of the hydroxyl group so that this value also appears reasonable.

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In the case of the alcohols having very long hydrocarbon chains another effect can be clearly seen from the experimental results. In the molecule of vapor the hydroxyl group is able to bury itself at least partially among the coils of the hydrocarbon tail, so that the surface energy of the vapor molecule decreases considerably, beginning with chains of five or six carbon atoms in length. With shorter chains than this, the hydroxyl group is probably fully exposed. Particularly interesting results which are in good agreement with the principle of independent surface action are found in the case of dibasic and tribasic alcohols. The heat of evaporation depends to a great extent on whether the separate hydroxyl groups are able to come into contact with each other in the molecule of vapor and thereby decrease the surface energy.

The theory can readily be extended to calculate the partial vapor pressures of binary solutions. The complete theory, taking into account orientation and segregation of molecules within the liquid, would be very complicated, but in many cases where the forces between molecules are not too strong, these effects can be neglected in a first approximation. Assuming then a random orientation and distribution of the molecules, the total surface energy per molecule in a solution of any given concentration in terms of interfacial surface energies, such as γ_{ac}, and surface fractions, such as a and c, the work done in transferring a molecule from a liquid to a vapor phase can then be calculated, and thus by applying the Boltzmann equation, it is possible to calculate the deviations from Raoult's law. Thus, the partial pressure of any liquid in a binary mixture is given by

$$p_A = AP_A \exp(\varphi S_A \beta^2/kT)$$

where p_A is the partial pressure of the substance A, the total pressure of the pure component A is P_A; the mole fraction of the component A is represented in this equation by A. The quantity S_A is the surface area per molecule of area; φ is a constant characteristic of the binary mixture but independent of the concentration of the components, which can be calculated in terms of such quantities as a, c, γ_{ac}, etc. The quantity β may be called the surface fraction of the component B in the binary mixture of A and B. It corresponds to the ordinary conception of mole fractions but is expressed in terms of the relative surfaces of the molecules instead of the numbers of the molecules. Thus

$$\beta = BS_B/(AS_A+BS_B)$$

This equation with only one adjustable constant, φ, apparently agrees in general better with experimental data than a somewhat similar equation with two adjustable constants derived by van Laar on the basis of thermodynamical considerations.

C. P. Smyth has recently used this equation in connection with his own measures of the vapor pressures of binary mixtures. The agreement, in most cases, is fairly good, but, as is to be expected in the case of more polar molecules, mixtures of alcohols with water show considerable deviations. It is probable

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that these can in large part be taken into account by developing the theory further to allow for orientation and segregation of the molecules within the liquid.

Views of the type which I have been discussing may thus be applied quantitatively, often with considerable accuracy, in studying the interactions between molecules of organic substances. The energy relations based on the conception of surface forces between molecules, together with the Boltzmann equation, frequently permit decisions to be made as to the mechanism of various surface phenomena. For example, in expanded films of oils on water it has often been assumed that the molecules could remain erect on the surface without touching one another. Simple energy considerations of the kind which we have been using indicate immediately that this is impossible. The tails of the molecules must remain in contact with each other in the case of long chains, but with shorter chains, the molecules may separate but must then lie flat upon the surface of the water. The principle of independent surface action affords one of the greatest safeguards against the setting up of impossible hypotheses.

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THE CRYSTAL STRUCTURES OF THE AMMONIUM HALIDES ABOVE AND BELOW THE TRANSITION TEMPERATURES

With GUY BARTLETT as co-author

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KNOWLEDGE of the geometrical arrangement of atoms in crystals, which is now available as a result of X-ray crystal analysis, should lead to more definite conceptions of the shapes of atoms and the forces around them. In a recent paper[1] it was pointed out from considerations of atomic structure, that the ions of sodium, potassium, fluorine and chlorine should have cubic symmetry while the ammonium ion, like methane, should have tetrahedral symmetry. This conclusion was thought to receive support from the difference in the crystal structures of potassium and ammonium chlorides. The halides of sodium and potassium have simple cubic lattices such as would be expected if the crystals were built up of alternate cubical ions of alkali and halogen with their faces in contact. Each ion is surrounded by 6 equidistant ions of the opposite polarity. Bragg[2] found that the ions in ammonium chloride are arranged in a centered cubic lattice so that each ion is surrounded by 8 equidistant ions of the opposite polarity. It was suggested that the "tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to faces or corners of the tetrahedrons." It was pointed out that the apparently complete isomorphism between ammonium and potassium sulfates is probably to be ascribed to the relatively large volumes of the sulfate ion.

Groth[3] gives potassium and ammonium chlorides as belonging to the same sub-group of the cubic system, the pentagon-icositetrahedric. Yet from evidence on the formation of mixed crystals it is concluded that these salts are not strictly isomorphous. However, a second form of ammonium chloride, stable only at high temperatures, is probably to be regarded as isomorphous with potassium chloride. Ammonium bromide was found to be isomorphous with ammonium chloride while the iodode is isomorphous with potassium chloride.

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[1] Langmuir, *J. Am. Chem. Soc.* **41**, 1547 (1919).

[2] W. H. Bragg and W. L. Bragg, *X-Rays and Crystal Structure*, London, 1916, p. 158.

[3] *Chemische Kristallographie*, Part I, Leipzig, 1906, p. 167.

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These relationships have been studied in detail by P. W. Bridgman,[1] who used pressures up to several hundred atmospheres and temperatures up to 200°. In this way he was able to discover a second modification of ammonium iodide analogous to those of the chloride and bromide. The transition temperatures at ordinary pressures are 184.3° for the chloride, 137.8° for the bromide and −17.6° for the iodide. Bridgman suggested that this new low temperature form of the iodide would be found to be isomorphous with the ordinary (low temperature) forms of the chloride and bromide.

These conclusions seem to be in accord with the conception of a tetrahedral symmetry for the ammonium ion. Thus at low temperatures, where the ions are packed more closely, the shape of the ammonium ion exerts a predominating influence and causes the lattice to assume the centered cubic form. At higher temperature, as the distances between the ions increase, the shape of the ammonium ions becomes of relatively less importance, and the lattice changes to the more common (for salts at least) simple cubic form.

Just as in the case of the sulfates of potassium and ammonium, the shape of the ammonium ion plays a smaller part when the anion is of large volume. Thus the greater the atomic volume of the halogen ion the lower the temperature at which the transformation takes place.

No data are available on polymorphism of ammonium fluoride but a consideration of Bridgman's data for the other ammonium halides suggests that the fluoride likewise may occur in 2 isometric forms, with a transition temperature higher than that of the chloride. Marignac[2] reported, however, ammonium fluoride as in the hexagonal system.

The following experiments were undertaken to determine definitely the relationships between the various ammonium halides, especially in regard to their crystal structure.

Experimental Results

By means of Hull's method[3] of X-ray crystal analysis the crystal structures of the following salts were determined: ammonium chloride at 20° and 250°, the bromide at the same temperatures, and the iodide at 20°. The calculations are based on the tables and formulas contained in Hull's article in the *Physical Review*.

Under ordinary temperature and pressure conditions the lattice of ammonium chloride crystals consists of 2 systems of intermeshed cubes of ammonium and chlorine ions. The corners of one of the series of cubes occupy the centers of the other series of cubes, giving a centered cubic arrangement of the

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[1] Bridgman, *Proc. Am. Acad. Arts Sci.* **53**, 91 (1916); see especially pp. 133–139 and 151–152.
[2] Marignac, *Ann. mines* [5] **15**, 221 (1859).
[3] A. W. Hull, *Phys. Rev.* **10**, 661 (1917); *J. Am. Chem. Soc.* **41**, 1168 (1919).

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ions (NH_4^+ and Cl^-), each being surrounded by 8 equidistant ions of the other kind. The length of the side of the elementary cube is 3.859 Å (one Ångstrom = 10^{-8} cm), and this is also the distance from any ion to the nearest ion of the same kind. The shortest distance between ions of opposite signs is 3.342 Å. The density calculated from this lattice is 1.536 in good agreement with the value usually given in tables, 1.520.

When the ammonium chloride is heated to 250° the structure changes, the lattice becoming simple cubic with alternate ammonium and chlorine ions, each ion being surrounded by 6 equidistant ions of the other kind. The unit spacing is 6.533 Å so that the nearest distance between ions of the same kind is 4.620 Å, while between ions of opposite kinds it is 3.266 Å. The calculated density is 1.265 at 250°, which is 15.7 per cent less than the density at 20°. Bridgman observed a decrease of density of about 13 per cent as the temperature was raised through the transition point.

Ammonium bromide is similarly affected by heat. At 20° the structure is centered cubic and the distance between like ions is 3.988 Å, while between unlike it is 3.453 Å. This gives a density of 2.548. Landolt-Börnstein gives 2.256 to 2.41. At 250° the structure is simple cubic, the distance between like ions being 6.90 Å, and between unlike ions 3.45 Å. The density is found to be 1.972 or 20.8 per cent less than at 20°. Bridgman found a decrease of density of about 14 per cent at the transition point.

The lattice of ammonium iodide at 20° is simple cubic like those of the high temperature forms of the chloride and bromide and like that of sodium chloride. The distance between like ions in ammonium iodide is 5.090 Å and between unlike ions 3.60 Å. The density is calculated to be 2.563 at 20°, while Landolt-Börnstein gives 2.443 to 2.501.

A photograph of the pattern given by ammonium chloride at 200° showed lines of both structures — the high and low temperature forms. This seems to be due to the slow rate of change when near the transition temperature. The rate of change was much increased by raising the temperature.

The results of the above X-ray analyses indicate that the structure of ammonium iodide at room temperature and of the chloride and bromide at high temperature are similar, simple cubic like the sodium and potassium halides; and that the crystal structure of ammonium chloride and bromide are alike at room temperature, centered cubic.

These results constitute very definite evidence in favor of the theory that the ammonium ion has tetrahedral symmetry while the alkali and halogen ions are cubic in shape.

Preparations are now being made for X-ray analyses of the structures of ammonium fluoride at room and high temperatures and of ammonium iodide at low temperature. It will probably be necessary to employ high pressures to obtain the low temperature form of ammonium iodide. It is probable that the structure of the fluoride at room temperature and of the iodide at low tem-

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perature will be like that of the chloride at room temperature, and that a high temperature form of the fluoride may exist corresponding to the high temperature form of the chloride.

In Hull's method of crystal analysis all the metallic elements which crystallize in any one of the 3 types of cubic lattice (simple cubic, centered cubic or face centered cubic) produce similar patterns. This is because the atoms of the crystal are all alike. In the analysis of salts, however, different results are obtained because of differing atomic numbers of the 2 or more atoms. Thus potassium chloride, simple cubic in structure, consists of ions containing the same number of electrons so that the pattern produced corresponds to that of a simple cubic lattice built up of atoms of one kind only. In sodium chloride, however, also simple cubic in structure, where the atomic weights of the 2 atoms are different, the pattern produced is that of a face-centered lattice of twice the linear dimension. This is because a simple cubic structure with alternate corners of different atoms can be resolved into 2 intermeshed face-centered lattices of twice the size, a lattice of each kind of atom. A salt having a centered cubic structure, when the atomic weights of the 2 elements are different, produces a pattern like that of an element in simple cubic arrangement (the same pattern as of potassium chloride), because a centered cubic arrangement is equivalent to 2 intermeshed simple cubic lattices, one lattice for each kind of atom.

The low temperature forms of the ammonium halides produce patterns of the potassium chloride type (simple cubic), although they are centered cubic in structure, because of the difference in atomic weights between the ammonium radical and the halogen atoms. The high temperature forms produce patterns of the sodium chloride type (face centered), although the ions are arranged in a simple cubic lattice having half the spacing of the face-centered lattice shown by the pattern.

In the case of ammonium fluoride it is expected that the patterns, because of the closeness of atomic numbers will be more nearly like those of elements having similar structure.

Experimental Data

The X-rays were obtained from a water-cooled Coolidge tube with molybdenum target. The rays, being filtered by a thin sheet of zirconium oxide and one of metallic molybdenum, had an effective wave length of 0.712 Å. The exposures were of 16 hours duration with 30,000 volts and 20 milliamperes. The radius of the film holder was 10.16 cm and duplitized films and calcium tungstate intensifying screens were used. The samples examined were finely powdered chemically pure salts sealed in thin-walled glass capillary tubes. Heat was applied by a small electrically heated coil placed just below the sample and parallel to it. The temperatures were estimated by substituting liquids of known boiling points for the salts in the capillaries.

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TABLE I

Ammonium Chloride at 20°

Simple cubic lattice		Unit spacing 3.860 Å	
Indices of plane	Relative intensity estimated	Spacing of planes	
		Observed	Calculated
110	10	2.718	2.730
111	1	2.238	2.228
200	2	1.924	1.931
210	1.5	1.725	1.727
211	3	1.568	1.576
220	1.5	1.362	1.365
221–300	1	1.287	1.286
310	1.5	1.214	1.221
311	0.8	1.162	1.163
222	0.8	1.111	1.117
320	0.6	1.073	1.071
321	1.8	1.024	1.031
400	0.3	0.958	0.965
410–322	0.6	0.935	0.936
411–330	0.8	0.912	0.910
331	0.5	0.891	0.886
420	0.5	0.867	0.863
421	0.5	0.844	0.842
332	0.5	0.822	0.823
422	0.4	0.787	0.788
430–500	0.3	0.772	0.772
431–510	0.7	0.755	0.757

TABLE II

Ammonium Chloride at 250°

Face-centered cubic lattice		Unit spacing 6.533 Å	
Indices of plane	Relative intensity estimated	Spacing of planes	
		Observed	Calculated
200	10	3.295	3.267
220	10	2.308	2.310
311	5	1.962	1.970
222	5	1.888	1.886
400	2	1.629	1.633
331	4	1.494	1.498
420	4	1.454	1.428
422	3	1.334	1.334
511–333	1.5	1.253	1.286
440	1	1.165	1.154
531	1.5	1.105	1.104
600–442	1.5	1.089	1.088
620	1	1.034	1.033
533	0.7	0.988	0.996
622			0.985

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The following tables give the relative intensities of the lines found on the 5 films and the spacings of the planes calculated from the lines. In most cases more than one film was taken but as these were essentially alike only the data from the films are recorded. The calculations were carried out in the way described by Hull. In every case the agreement between the observed and calculated spacings of the planes is very close and is sufficient to prove definitely the correctness of the assumed structure. The films obtained with ammonium chloride and iodide gave sharp and distinct lines so that a relatively large number of lines were observed. With ammonium bromide, however, the films were rather badly fogged by secondary radiation from the bromine

TABLE III

Ammonium Bromide at 20°

Simple cubic lattice		Unit spacing at 3.988 Å	
		Spacing of planes	
Indices of plane	Relative intensity estimated	Observed	Calculated
110	10	2.832	2.820
111	2	2.303	2.303
200	2	1.991	1.955
210	4	1.785	1.783
211	4	1.639	1.629
220	2	1.413	1.410
221–300	2	1.327	1.329
310	2	1.261	1.261
311	1.5	1.191	1.202
222	1	1.164	1.152
320	1	1.105	1.106
321	1.5	1.059	1.066

TABLE IV

Ammonium Bromide at 250°

Face-centered cubic lattice		Unit spacing 6.90 Å	
		Spacing of planes	
Indices of plane	Relative intensity estimated	Observed	Calculated
200	10	3.440	3.449
220	10	2.439	2.439
311	8	2.082	2.080
222	4	1.990	1.992
400	2	1.750	1.725
331	6	1.585	1.582
420	6	1.543	1.543
422	4	1.420	1.408
511–333	4	1.330	1.327

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TABLE V

Ammonium Iodide at 20°

Face-centered cubic lattice		Unit spacing 7.199 Å	
Indices of plane	Relative intensity estimated	Spacing of planes	
		Observed	Calculated
220	10	2.531	2.545
311	10	2.168	2.171
222	3	2.086	2.078
400	2	1.797	1.800
331	8	1.652	1.652
420	8	1.607	1.610
422	5	1.471	1.470
511–333	4	1.385	1.386
440	2	1.268	1.273
531	4	1.224	1.217
600–442	4	1.201	1.199
630	2	1.141	1.139
533	1.5	1.095	1.097
622	1.5	1.083	1.085
444	0.5	1.041	1.039
711–551	1.5	1.010	1.008
640	..	...	0.998
642	1	0.966	0.962
553–731	1	0.936	0.937

excited by the rays from the molybdenum target. This might have been avoided by using an X-ray tube having a different target material. However, since the number of lines observed was sufficient to establish the structure of the crystals no effort was made to overcome this difficulty.

Summary

Ammonium chloride, bromide and iodide exhibit polymorphism and have well defined transition temperatures. X-ray crystal analysis by Hull's method shows that the high temperature form of each of these salts has a simple cubic structure like sodium chloride, each ion being surrounded by 6 equidistant ions of the opposite polarity. The ordinary or low temperature forms of the chloride and bromide show a centered cubic structure, each ion being surrounded by 8 equidistant ions of the opposite polarity, arranged as the corners of a cube about its center. These results furnish confirmatory evidence that the ammonium ion has tetrahedral symmetry while the alkali and halogen ions are cubic in shape. Low temperatures, high pressures and anions of small atomic volume cause the shape of the ammonium ion to be a factor of predominating importance in determining the crystal structure. High temperatures, low pres-

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sures and anions of large volume make the shape of the ammonium ion of relatively less importance so that under these conditions ammonium salts tend to become isomorphous with the corresponding potassium salts.

The numerical data relating to the crystal structures of the ammonium halides are given in the following table.

TABLE VI

Summary of Results

Salt	Temp. °C	Arrangement of ions	Distance between like ions. Å	Distance between unlike ions. Å	Density (calculated)	Molecular volume
NH_4Cl	20	Centered cubic	3.859	3.342	1.536	34.9
NH_4Cl	250	Simple cubic	4.620	3.266	1.265	42.3
NH_4Br	20	Centered cubic	3.988	3.453	2.548	38.4
NH_4Br	250	Simple cubic	4.88	3.45	1.972	49.7
NH_4I	20	Simple cubic	5.090	3.60	2.563	56.6

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VECTOR MAPS AND CRYSTAL ANALYSIS

With Dr. Dorothy Wrinch as co-author

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In a series of communications, Patterson[1] and Harker[2] have introduced a new method of exhibiting the data contained in X-ray photographs of a crystal with the view of facilitating the use of such data for the determination of the atomic arrangement in the crystal. The essential feature of this type of analysis lies in the use of special Fourier series by means of which it is theoretically possible to construct a three-dimensional "vector" map of a crystal, regarded as a distribution in space of positive and negative point intensities, superposed upon a continuously varying volume distribution of electrons. These maps represent, not the distribution of the point intensities in space, which is of course the objective of crystal analysis, but vector distances between them taken two at a time. The question then arises as to how far it is possible to derive from point intensity distributions in "vector" space, S_2, corresponding point intensity distributions in "atomic" space, S_1.

Vector diagrams, that is, sections and projections of vector maps, have been constructed in a few cases including proustite[2], pyrargyrite[2], and pentaerythritol[3]. Supplemented by data relating to the chemical composition, density, etc., of the crystal, they have been used in the determination of these structures. Some vector diagrams have also been constructed for an insulin crystal[4].

Previous to the construction of these diagrams, a structure, namely, the cyclol cage C_2, was proposed for the insulin molecule[5]. Investigations were consequently undertaken[5,6] to ascertain whether these diagrams confirm this structure or (as has been stated[4,8]) fail to confirm it, in the course of which it became clear that simple geometric arguments make it possible to go a long way towards interpreting these diagrams, and presumably other vector diagrams also, even when nothing whatever is known about the chemical composition, size, shape or density of the insulin molecule. In this communication a preliminary sketch is given of the geometrical method developed in these investigations, since it appears to have a wide field of applicability in the interpretation of vector maps, whether they are derived from molecular or megamolecular lattices.

We consider first vector maps which result from various simple distributions of point intensities. Suppose in atomic space S_1 there are two points A, B with intensities $\pm r$, $\mp s$ respectively. To construct the vector map in space S_2 of

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this distribution in S_1, we select any point O as origin in S_2 and erect at O vectors corresponding to the vector distances from A to A, from B to A, from A to B, and from B to B, associating with AA, BA, AB and BB, the end points of these vectors, intensities r^2, $-sr(=-rs)$, $-rs$ and s^2 respectively. We may write this result in the form

$$V(\pm rA \mp sB) \equiv (\pm rA \mp sB, \quad \pm rA \mp sB) = r^2AA - srBA - rsAB + s^2B^2 \quad (1)$$

Here the points AA and BB lie at the origin O, and since the steps from B to A and A to B in S_1 are equal and opposite, the points BA and AB in S_2 are symmetrically placed with respect to the origin. We notice that points in S_2 obtained from pairs of points in S_1 with intensities of the same sign have positive intensities, those obtained from pairs of points in S_1 with intensities of opposite signs, negative intensities; also that the magnitude of the intensity at O is the sum of the squares of the intensities of the points in S_1.

Now the expression on the right of (1) is the formal expansion of the expression $(rA-sB)^2$, and the generalized expression

$$V(\sum_n r_n A_n) \equiv \sum_n r_n^2 A_n A_n + \sum_{m \neq n} r_n r_m A_n A_m \quad (2)$$

similarly gives the method of constructing vector maps for any set of point intensities in any dimensions. This binomial formulation of the structure of the vector map of a set of points not only makes it simple and easy to be sure that all the requisite terms have been considered: it also indicates the type of mathematical problem upon the solution of which the interpretation of vector maps depends. It is essentially akin to the problem of finding a square root; indeed interpretation of vector maps is the art of deducing the positions of n points in space S_1, from the positions of n^2 points in S_2.

To apply these ideas to crystals, we consider distributions of point intensities which are periodic. Thus if in S_1 there is a one-dimensional distribution, consisting of points of intensity $\pm r$ alternating with points of intensity $\mp s$ at even distances, the vector map in S_2 has the same unit cell and comprises at cell boundaries an intensity of r^2+s^2 and at midpoints intensities of $-2rs$.

A second illustration — a two-dimensional crystal in which the unit cell is rhombic — is shown in Fig. 1*a*. The repeating unit consists of a hexagon of points of intensity $\pm r$, at the centre of the hexagon a point of intensity $\mp s$, in addition a point of intensity $\pm t$, arranged as shown. The vector map, periodic in the same unit cell, is shown in Fig. 1*b*. It contains points with intensities $2r^2$, r^2, $2r^2-2rs$, $2rt-2st$. (In the figures, relative intensities are indicated by the areas of the circles. They have been drawn for the particular case in which in S_1 $r:-s:t = 8:-6:3$, so that the intensities in S_2 are in the ratio $2r^2:r^2:2r^2-2rs:2rt:-2st = 32:16:8:12:-9$.)

A third example relates to a three-dimensional crystal in which the rhombohedral cell contains one molecule consisting of points of intensity $\pm s$ at the

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corners of an octahedron and a point of intensity $\mp o$ at its centre. The molecules are arranged with one trigonal axis along the trigonal axis of the crystal. Fig. 2*a* shows the *c*-plane projection of the crystal in S_1. Fig. 2*b* shows the corresponding projection of its vector map in S_2, in which there are points the intensities of which are $2s^2$, s^2 and $2s^2-2os$.

The S_2 projection shows that the molecules in S_1 are trigonal and that the molecular and crystal hexagonal axes are not coincident but make an angle with one another (say 6° in the figure). The dimensions of the molecule are obtained when it is realized that the distribution around the cell corners in S_2 implies a distribution around the cell corners in S_1 of half the dimensions. The relative intensities of the points *A*, *B* (s^2 and $2s^2$ respectively) make it possible

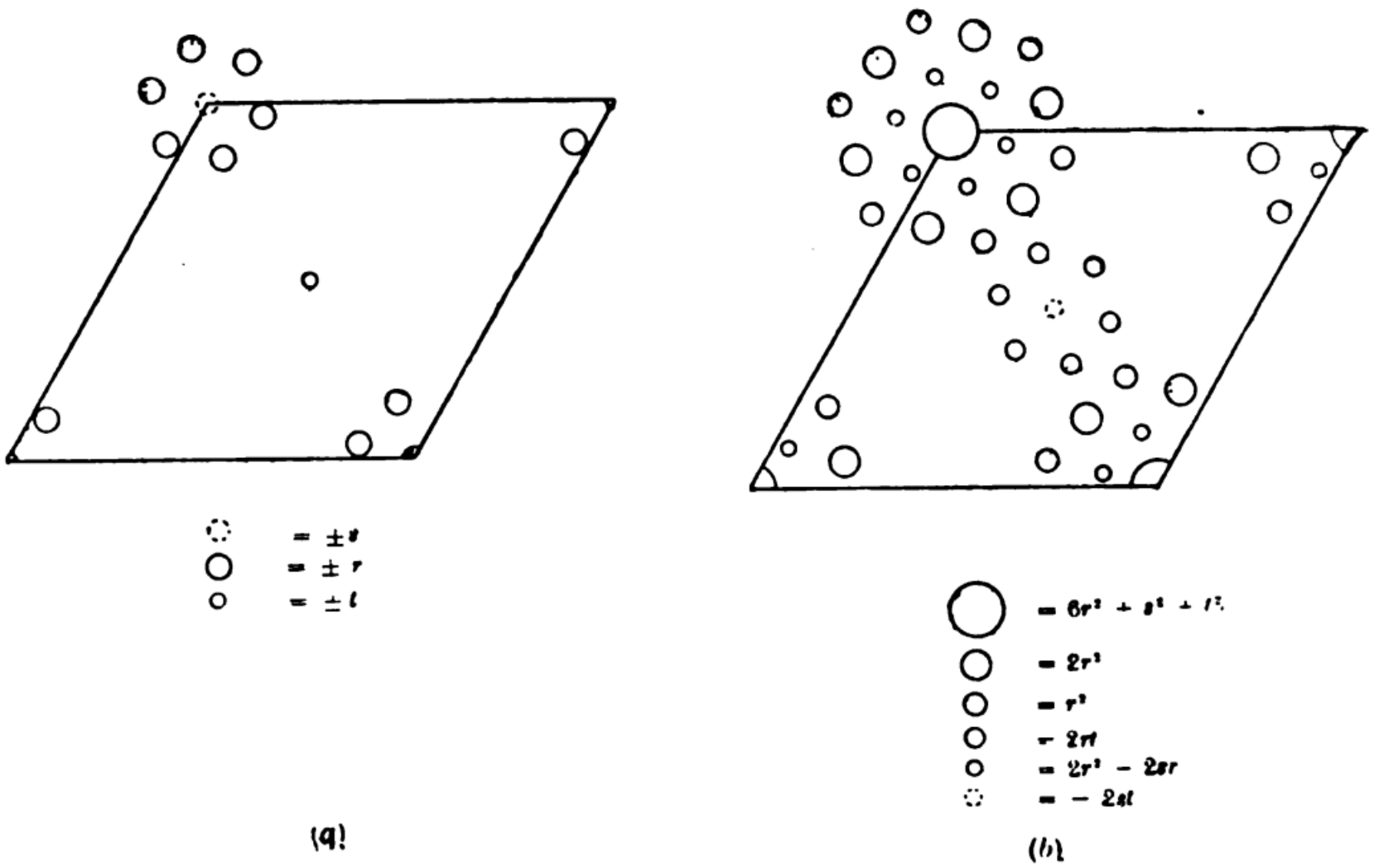

FIG. 1.

to interpret the intensities on an absolute scale. Finally, the lower intensity of the point *C*, which contains a term $2s^2$, demonstrates the presence of an intensity at the centre of the molecule the sign of which is opposite to that of *s*, which, contributing, with the *s* points, a negative intensity $-2os$ to *C*, reduces the total intensity there to $2s^2-2os$.

The illustrations given above have been selected, not only because they indicate the essentials of the geometrical method of approach to the problem of interpreting vector maps, but also because they are directly relevant to the case of insulin. Thus, in Fig. 2*b*, the positions of the maxima *A*, *B*, *C* found in the *c*-plane projection of the vector map of an insulin crystal calculated from X-ray photographs are reproduced[9]. The points associated with the hexagons

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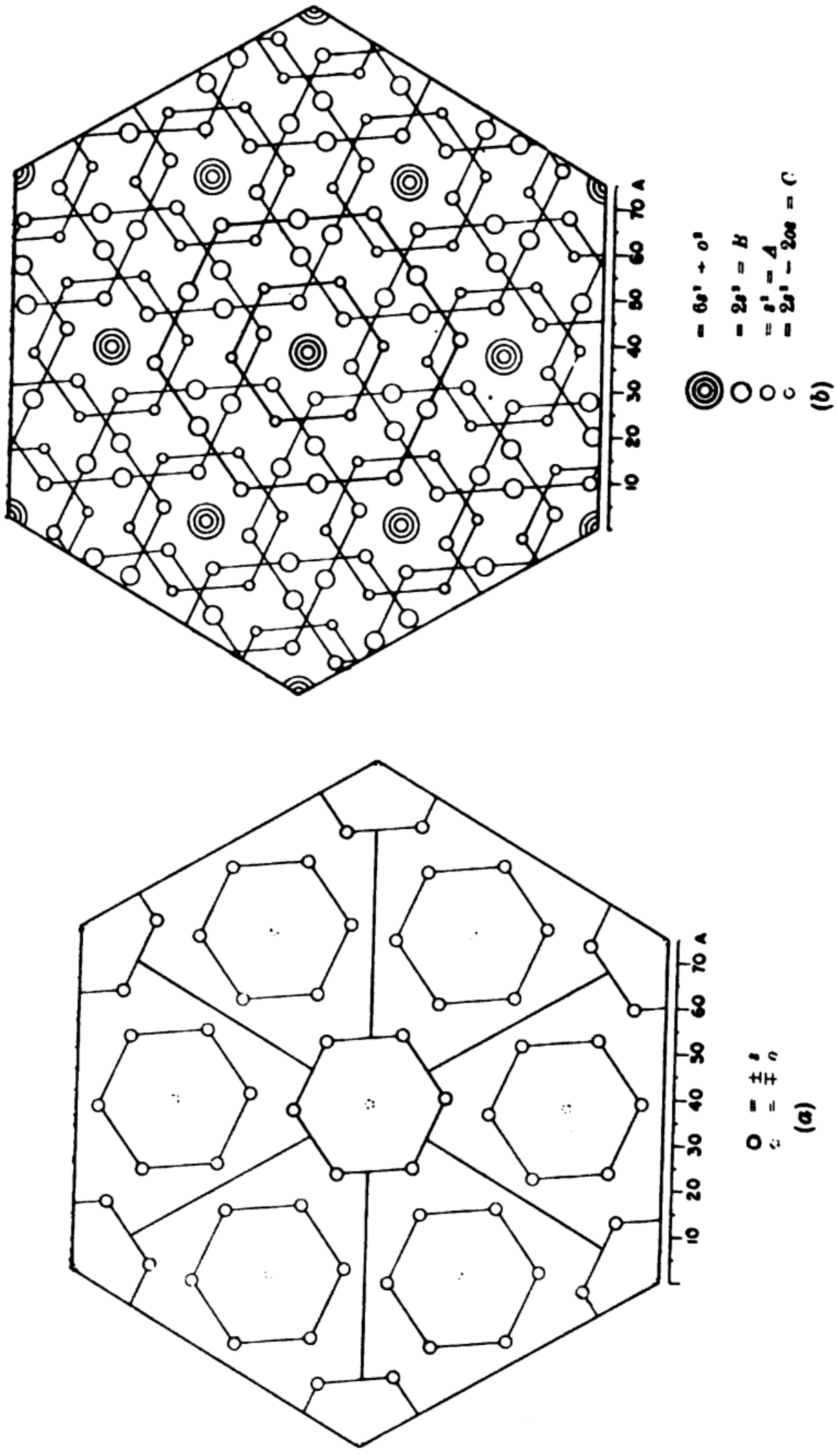

FIG. 2.

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obtained from the C_2 cages are also shown. The superposability of these two sets of points represented the first stage in the proof of the correctness of the C_2 structure proposed for insulin[6]. Fig. 2*a* indicates the size and orientation of the molecules in the insulin lattice, deduced from the vector diagram, Fig. 2*b*.

Again, Figs. 1*a* and *b* show how it proved possible[7] to deduce from the vector section, $z = \frac{1}{2}$[10], the presence and position of three "foreign" high intensity points per molecule in the lattice, nothing whatever being assumed about the chemical composition of the crystal. The images in Fig. 1*b* around the cell corners and around the middle point of the cell of the original distribution around the corners of the cell in Fig. 1*a* show how the existence and size of the negative intensity region at the centre of the insulin molecule was also deduced from this section[7]. These investigations, showing that it is possible to deduce that the insulin molecule is a polyhedral cage structure of the shape and size predicted, give some indication of the powerful weapon which the geometrical method puts at our disposal.

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THE ROLE OF ATTRACTIVE AND REPULSIVE FORCES IN THE FORMATION OF TACTOIDS, THIXOTROPIC GELS, PROTEIN CRYSTALS AND COACERVATES

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The formation of tactoids from thixotropic sols, of Schiller layers from iron-oxide sols, the separation of tobacco virus solutions and bentonite sols into two liquid layers and the crystallization of proteins are regarded as examples of unipolar coacervation (micelles having like charges) which must involve attractive forces.

Kallmann, Willstäter, Freundlich, De Boer, Hamaker, Houwink and others have assumed that the attraction is due to van der Waals forces. They have also analyzed the stability of colloid systems by diagrams giving the potential energy as a function of the distance between micelles. It is now shown that the Coulomb attraction between the micelles and the oppositely charged ions in the solution gives as excess of attractive force which must be balanced by the dispersive action of thermal agitation and another *repulsive* force. Thus there is no need to assume long range van der Waals forces. The past use of energy diagrams is criticized because it has ignored the effect of the thermal agitation and the attraction of the "gegenions" in solution. Instead of potential energy it is proposed that osmotic pressure p be used, which includes these previously neglected factors. A maximum in p as the colloid concentration increases is the condition for the separation into two phases (coacervation).

The Debye-Hückel theory (1st approximation) for the osmotic pressure of electrolytes takes into account both these factors and permits a rough calculation of the conditions under which coacervation occurs. The 2nd approximation, which considers particle size, does not agree as well with experiment as the first approximation. The reasons for this lack of agreement are discussed.

The micelles in unipolar coacervates are not in contact, but are separated by relatively large distances (10–5000A). Either a specific repulsive force or a decrease in the Coulomb attraction as the concentration increases (due to decreased charges on micelles) can account for stable coacervates. The assumption of a definite ζ-potential, rather than a definite charge on the micelles, gives automatically just such a decrease in attraction.

The general mathematical theory of coacervation presents great difficulties because the approximations of the Debye-Hückel theory cannot be used. However, the one-dimensional problem of the forces acting between parallel colloidal platelets can be solved rigorously in terms of elliptic integrals. For highly charged particles in sufficiently dilute solutions of electrolytes, the pressure p in the liquid between the two plates is given by $p = (\pi/2)D(kT/eb)^2 = 8.9\times10^{-7}/b^2$ dynes/cm^2 where b is the distance in cm between the plates and D is the dielectric constant (81 for water at $T = 293°$K). This pressure which tends to force the plates apart is independent of the charge on the plates and on the electrolyte concentration (univalent ions only). Polyvalent ions decrease the force. This force is of the right magnitude to account for the stability of unipolar coacervates It also furnishes a quantitative explanation of the Jones-Ray effect, by which low salt concentrations decrease the capillary rise in surface tension experiments with water.

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Experimental determinations were made of the relaxation times τ for the decay of birefringence in bentonite and vanadium pentoxide sols, after stirring was stopped. In one sample of bentonite, τ varied with the 22nd power of the concentration, while in V_2O_5 sols the exponent was 1.8. The temperature coefficients of τ were also measured and the activation energies were calculated.

A theory of the relaxation of birefringence was developed, according to which the micelles in dilute thixotropic bentonite sols are arranged normally in a cubic lattice (isotropic). Temporary shear in the liquid orients the micelles and produces birefringence although the lattice remains cubic. The experimental data confirm the theory and indicate that the energy barrier opposing reorientation of micelles in a particular bentonite sol varied with the inverse 20th power of the distance between the micelles. With V_2O_5 this exponent was about 4. Further support for the theory was obtained by experiments which have "angles of isocline" for bentonite particles in a flowing sol that varied from 65° to 78°.

In bipolar coacervated (which contain micelles of unlike polarities) the electric fields and the charges on the micelles *increase* as the micellar concentration increases. When a certain concentration is reached, the field rises to a value so high as to cause increased hydration which holds the micelles apart and gives stability to the coacervate.

WHEN a solution of pure tobacco mosaic virus containing about 2 per cent of the protein is allowed to stand for several days, it separates into two phases.[1-5] The lower one, which is the more concentrated, is strongly doubly refracting and consists of a three-dimensional mosaic of small uniaxial liquid crystals arranged in random orientations with respect to each other. The top layer scatters much more light than the lower and is isotropic if undisturbed, but shows double refraction when subjected to shear (streaming double refraction).

During the separation of the liquid into the two phases, spindle-shaped or needle-shaped regions of low or high density, which slowly rise or fall in the solution, appear. The heavier masses which form in the upper part settle to the lower part and there coalesce with one another and with the surrounding liquid which has been enriched in protein by the removal of the lighter masses that have risen into the upper part. In this way the solution gradually separate. into two layers which at first have an indistinct transition between thems Gradually, however, the boundary becomes so sharp that it shows distinct total reflection when viewed from a position slightly below the plane of the boundary.

The upper phase in which thermal agitation rapidly brings about a random orientation of the molecules behaves as a slightly viscous, isotropic liquid. If, however, the liquid is made to flow, the shear causes a temporary parallel orientation of molecules, which decays, after the motion stops, with a relaxation time of the order of a second.

The lower phase is a thixotropic gel, which if undisturbed is essentially a solid body made up of uniaxial crystal grains. The more concentrated the original

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solution, the finer is the observed grain size. The mechanical strength of this gel is very low, for a shearing stress of the order of 10 dynes/cm² causes flow. The gel is liquefied by more vigorous stirring, but on standing sets again to a gel and remains birefringent.

X-ray examination[1,2] has shown that in the lower phase the rod-shaped virus molecules are arranged in a hexagonal close-packed lattice of parallel cylinders. The distance between adjacent molecules decreases continuously from about 500A to about 125A as the concentration of the protein in the solution increases.

The rod-shaped molecules are presumably held in position in the hexagonal lattice by repulsive forces resulting from negative charges on the protein molecules. According to the Debye-Hückel theory the force acting on a charged particle at a distance r from another charged particle is equal to the Coulomb force multiplied by an exponential factor, $\exp(-r/\lambda_D)$, where λ_D, which we may call the Debye distance, varies inversely as the square root of the ionic strength of the electrolyte. Thus the conditions under which the two-phase system forms and the spacing of the molecules in the more concentrated phase should be influenced in marked degree by the presence of electrolytes.

The properties of these tobacco virus solutions appear to be similar in many ways to those exhibited by certain thixotropic sols that have been studied by Zocher, Freundlich, Heller and others.[6–9]

Some thixotropic sols, such as those of V_2O_5, which contain rod-shaped crystalline particles, spontaneously form "tactoids", which are small, sharply defined, spindle-shaped, doubly refracting masses having higher density than the surrounding sol.

Some sols of iron oxide, having disk-shaped particles, when allowed to stand in a vessel with a flat bottom, may yield a separate denser phase in the form of an iridescent layer on the bottom of the vessel. When examined by white light the reflected light is found to be nearly monochromatic. The plate-like particles are thus arranged in parallel layers (Schiller layers) having a uniform spacing which may be as great as 8000A (giving a third-order red reflection).[9]

It has been generally assumed that the forces that hold these Schiller layers apart and the particles of tactoids apart, even at these relatively great distances of several thousand A, are electrostatic forces resulting from the large charges on the colloidal particles.

The properties of the tobacco virus solutions and their behavior during the separation into the two phases show that the phenomena are essentially the same as those involved in the formation of tactoids. In the virus solution,

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however, the "particle" is a protein molecule of molecular weight of about 50,000,000, while in the V_2O_5 sols the particles are needle-like crystals of much larger size.

Bentonite Sols

The monodisperse sols of bentonite that have been prepared by Hauser and Reed,[10] particularly the fractions having the smallest particle size are remarkably thixotropic, and, in the presence of minute concentrations of salts, are rheopectic. These sols seem particularly suitable for studies of the nature of the forces that act between colloidal particles. Traces of thixotropic behavior have been observed[10] in presence of salts at concentrations as low as 0.05 per cent where the average distance between the particles is of the order of 2000A.

Mr. V. J. Schaefer and I have recently studied some bentonite sols that were prepared in Dr. Hauser's laboratory by Dr. F. J. Norton. The sample that we used was a monodisperse sol whose equivalent spherical diameter was about 300A. These sols were made from a white California bentonite whose analysis gave: SiO_2 39.2 per cent; Al_2O_3 0.11 per cent; Fe_2O_3 0.15 per cent; CaO 15.1 per cent; MgO 19.2 per cent; ignition loss 22.7. Eighteen different dilutions of a single sample of this sol were made up with concentrations ranging from 0.8 to 2.8 per cent (as determined by drying at 105°C). Volumes of 4 ml. of each of these solutions were sealed into glass tubes about 0.8 cm inside diameter.

These tubes were shaken and then tilted so that the bubbles passed slowly the length of the tube. They were then placed in a rack and were examined between crossed Polaroids while they were standing undisturbed in a vertical position.

The solutions that contained less than 1.4 per cent became isotropic within a couple of seconds, while the birefringence of the more concentrated solutions persisted for a time τ which increased rapidly with concentration. The sol containing 1.40 per cent gave $\tau = 3$ seconds and this increased to 12 seconds at 1.50 per cent, to 40 seconds at 1.57 per cent and to 80 hours at 1.8 per cent. The sol containing 2 per cent after several hundred hours become isotropic in its upper half, while the lower half remained permanently birefringent, showing a fine mosaic structure of crystal grains having optic axes inclined about 45° to the axis of the tube. With the tube containing the sol of 2.2 per cent a sharply defined isotropic portion of about 6 cm depth separated out at the top of the tube. The lower part consisted of the fine grained crystal mosaic. The sols of still higher concentrations appeared to be permanently crystalline throughout. It was only in the concentration range of 2.0 to 2.2 per cent that two distinct phases separated after long standing.

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[10] E. A. Hauser and C. E. Reed, *J. Phys. Chem.* **40**, 1169 (1936); **41**, 911 (1937).

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The sols that contained from 1.4 to 2.0 per cent were thixotropic gels which on standing slowly increased in strength so that (above 1.50 per cent) even large bubbles would not move through them when the tubes were inverted. After standing a sufficient length of time, the gels lost their birefringence and became isotropic, but if these gels were shaken very gently or made to oscillate about a horizontal axis they showed temporary birefringence, which disappeared as soon as the agitation stopped. They thus acted essentially like solid elastic bodies which become birefringent when subjected to stress. If the tubes were vigorously shaken, the gel liquefied, and the liquid became anisotropic. It is clear therefore, that, in the case of the bentonite sols, birefringence and the mechanical strength of the gel are not closely associated. With tobacco virus solutions, however, the thixotropy and spontaneous birefringence go together.

It has often been thought[3, 5, 8] that the property of separation into two phases, one of which is isotropic and the other permamently birefringent, is characteristic only of sols having rod-shaped particles. The optical properties of the bentonite sols, however, prove that the particles are flat plates or disks.

It is probable that the repulsive forces between the particles in the bentonite sols, at concentrations above 1.4 per cent, cause these particles to assume a lattice-like arrangement (probably a close-packed face-centered cubic type), which gives to the sol its elastic or gel-like properties. This ordered arrangement must start from nuclei and spread to give grain-like lattice regions separated by diffuse boundaries of unordered particles. A very slight shearing motion in the liquid can rotate the grains and allow them to coalesce and so grow in size (rheopexy), but too great a shearing stress disrupts the grains and causes the gel to become liquid (thixotropy).

Although the center of each particle may thus occupy a definite position in a crystal lattice, the disk-shaped particle, at low concentrations, can rotate freely in all directions. With increasing concentrations, however, the potential energy will be a minimum when the disks have definite orientations.

Let us consider, for example, that the particles are negatively charged, electrically conducing disks arranged in a face-centered cubic lattice, with the appropriate number of univalent positive ions distributed in the aqueous phase in accord with the Poisson and Boltzmann equations. Each particle has 12 equidistant neighbors arranged like the midpoints of edges of a cube about its center. Symmetry considerations seem to indicate that the potential energy of conducting disk will be a minimum when the axis of the disk lies parallel to any one of the three cubic axes of the lattice.

The induced charges on the disk then cause it to act as an octupole and for other orientations there will be even more poles. The energy barrier that must be overcome if the axis of the disk is to pass from one equilibrium position to another must thus increase with some high power ϱ (such as 10 or more) of the ratio d/r, where d is the diameter of the disk and r the distance between

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the centers of neighboring disks. If the disks are not circular, or if they carry permanent dipole moments, ϱ will be reduced, and the magnitude of the energy barrier increased.

Let us use this model in analyzing the changes in properties of bentonite sols that occur with increasing concentration, n, of the particles per cm³. At very low values of n where the particles are now in lattice positions, there is no energy barrier to oppose free rotation. The Brownian rotation (average angle θ, in time t) should be given approximately by Einstein's equation

$$\theta^2 = kTt/4\pi\eta a^3, \tag{1}$$

where η is the viscosity of the solvate and a the effective radius of the particle (assumed spherical).

The effective diameter of the particles of the bentonite sols we have made, calculated from the sedimentation rate by Hauser's method[10] was 300A. If the particles are thin circular disks of diameter d and thickness b, the effective diameter d_e should be roughly of the order of magnitude of the geometric mean of d and b. If we take $b = 20$A, which is the spacing of layers in wet clay minerals given by x-ray measurements, we get $d = 4500$A, or 0.45μ.

By Eq. (1) for $\eta = 0.01$, $a = 2.25 \times 10^{-5}$, we find $t = 0.04\theta^2$ second. Thus if the particles are oriented by artificially produced laminar flow in the liquid, this orientation disappears in a small fraction of a second. The relaxation time of about one second which we observed for bentonite concentrations of 0.8 to 1.2 per cent may have been due to the persistence of motion in the liquid after passing the bubble through the tube.

The increased time of 3 seconds at 1.4 per cent, however, could not have been due to this cause, for the greater viscosity should have decreased the duration of flow. Thus at concentrations of about 1.4 per cent the energy barrier has become great enough to interfere with free rotation. At higher concentrations the axes of the disks normally oscillate about equilibrium positions parallel to the 3 lattice axes, but occasionally pass over a barrier to other equilibrium positions with a relaxation time τ given by

$$\tau = A\eta \exp(Ve/kT), \tag{2}$$

where V is the height of the energy barrier in electron volts, A is a constant and η is the viscosity. Since the rotation of a micelle does not appreciably alter the positions of other micelles, η should be the viscosity of the solvate (water) rather than that of the solution and should thus be independent of the concentration of bentonite.

We may assume that V varies inversely with the ϱth power of the distance r between molecules,

$$V = Br^{-\varrho}. \tag{3}$$

By logarithmic differentation of Eq. (2), remembering that the concentration n varies in proportion to r^{-3}, we obtain

$$d\log\tau/d\log n = (\varrho/3)(Ve/kT) = 3870\varrho V/T, \tag{4}$$

if V is in volts.

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The increase in τ from 3 to 40 seconds for an increase in concentration from 1.40 to 1.57 per cent, which we observed for bentonite sols, corresponds to a value of $d \log \tau / d \log n = 22.4$ and thus we obtain, at 20°C, $\varrho = 1.70/V$.

The value of V can be determined by Eq. (2) from the temperature coefficient of τ. The sealed off tube containing 1.4 per cent of bentonite which had been used for the first determinations of τ was immersed in ice water, the tube was tilted so that the bubble traveled half the length of the tube and back and was replaced in the ice bath. The anisotropy between crossed Polaroids disappeared[11] after 220 seconds. When this was repeated with the tube immersed in water at 40°C the time for the disappearance of anisotropy was 50 seconds.

This 4.4-fold increase in rate for 40°C, or 1.45-fold for 10°C, corresponds to a total activation energy of 6.3 kcal. per mol or an energy barrier of 0.274 volt. But by Eq. (2) we see that we must subtract the activation energy (4.3 cal. or 0.184 volt) which determines the temperature coefficient of the viscosity of water (decrease from 0.01793 to 0.00657, ratio 2.73:1, between 0° and 40°). Thus we find the energy barrier for rotation of the particles in the 1.4 per cent bentonite sol is $V = 0.084$ volt. Combining this with our previous result $\varrho = 1.70/V$, we find that the exponent ϱ in Eq. (3) should be $\varrho = 20$. This high value is reasonable for charged nearly circular conducting disks and indicates that the orientation of the particles is not caused by permanent dipole moments on these particles. The energy barrier V varies with the $\varrho/3$ or 6.7 power of the concentration. Thus taking $V = 0.084$ volt at 1.4 per cent we obtain $V = 0.03$, 0.05, 0.13 and 0.21 volt at concentrations of 1.2, 1.3, 1.5 and 1.6 per cent respectively.

The development of permanent anisotropy and the separation into two phases which was found to occur at concentrations of 2.0 to 2.2 per cent appears to be due to a mutual orienting effect of neighboring disks, which becomes important at high concentrations. The axes of all the disks in a crystal grain thus become parallel, and this alters the forces of interaction between the disks so that a new kind of uniaxial crystal grain is formed having a higher density, leaving a less concentrated isotropic intergranular material.

At concentrations above 2.4 per cent the stiffness of the sol was apparently too great to permit the separation of the phases, but microscopic examination would probably have shown the isotropic phase between the crystal grains. A slight rocking or tapping motion would probably accelerate the separation into phases (rheopexy), or moderate centrifugation could be used.

[11] This determination of the temperature coefficient of τ was made about four months after the solutions were sealed into the glass tubes. There had been a gradual change in the properties of the sols during this time, probably due to traces of substances taken up from the glass. During this time the value of τ for the tube containing 1.4 per cent increased from 3 to about 100 seconds and similar increases were found with the other tubes. The property of giving two phases after long standing, which was originally observed with the 2.0 and 2.2 per cent sols, was also gradually lost. These properties of bentonite solutions are extremely sensitive to traces of salts and other substances.

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According to these views, the birefringence of the bentonite sols is due to orientation of anisotropic bentonite particles rather than to a dissymmetry of the crystal lattice. The isotropic gels obtained by allowing the sols of concentration less than 2 per cent to stand quietly for a time τ are birefringent (instantaneously reversible) when subjected to slight shearing stress (below their elastic limit). If, however, the intensity of the stress exceeds a critical value, permanent shear occurs and the anisotropy then decays slowly with the usual relaxation time τ.

These phenomena prove that the axes of the disks in the isotropic gels are not arranged in random directions, but oscillate about definite *equilibrium axes* which are related to the crystal axes. The effect of a small shearing stress is to displace the equilibrium axes with respect to the crystal axes. Because of the large value of the exponent ϱ of Eq. (3) only a very slight distortion of the cubic lattice will be needed to give considerable angular displacements.

If the shearing stress is made sufficiently great, slip planes develop in the lattice and permanent displacement results. Because of the crystal lattice the direction of shearing displacement does not generally coincide with direction of the shearing stresses.

If the gel is subjected to continuously increasing displacements or flow, the gel structure is not necessarily completely broked down. With any given rate of shear a balance will be reached between the rate of growth of crystal lattice and the rate of destruction.

During this flow the disk-shaped particles become oriented under the influence of two factors. First, the solvate that surrounds the particles is subjected to laminar flow, probably parallel to the slip planes. This tends to orient the planes of the disks parallel to the slip planes. Second, between slip planes, there are distorted lattice arrangements in which the disks take an orientation different from either the direction of the shearing stress or the direction of the slip.

The following simple experiments show that the planes of the bentonite disks do not coincide with the direction of shear and so prove a crystalline structure even in the flowing liquid.

A 2 per cent sol of white bentonite was sucked up into a pipette and allowed to flow steadily into a beaker. The birefringence of the sol flowing down through the vertical tubular part of the pipette (8 mm inside diameter) was observed by placing the tube between a pair of crossed Polaroids. These were held by a frame which permitted them to be rotated about a horizontal axis perpendicular to their plane.

When the two planes of polarization made angles of 45° with the direction of flow, the sol gave good transmission along two side bands separated by a darker central band. With lower concentration, 0.8 to 1.2 per cent, the central dark band along the tube axis was more distinct than with the higher concentration.

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The presence of a dark central band is characteristic of particles which are disks or flat plates. Rods become oriented in the direction of flow which is also the direction of shear, and so give transmission over the whole width of the tube. Disks or plates in a noncrystalline liquid should become oriented with their planes parallel to the tube axis, but perpendicular to the radius of the cylinder through the particle, for these planes are tangent to the surface of shear.

If the particles are circular disks, they should not change the plane of polarization of light passing through the axis of the tube and thus there should be a black band in the axis when the crossed Polaroids are at 45°. If, however, the particles are plates which are longer than they are broad, so that their long axes are oriented parallel to the tube axis, the intensity of the central band should serve as a measure of the ratio of width to length.

Rough observations with 1 per cent bentonite sols show that the central band has an intensity perhaps half that of the side bands. This, with our previous observations of scattering, would indicate that the particles are thin flat plates of irregular shapes having lengths which are not large multiples of the widths.

When a vertically flowing sol is observed between crossed Polaroids having vertical and horizontal planes of polarization, one should expect to get no transmission with either rodshaped or disk-shaped particles. Actually, however, the 2 per cent bentonite sols show distinct transmission (perhaps $\frac{1}{4}$ as intense as with 45° Polaroids) in two side bands with a narrow completely black band between them. If the Polaroids are rotated slightly to the right (clockwise), the central black band moves to the right and becomes broader until at a Polaroid rotation of 12° the whole right side of the tube appears uniformly black, while the left side has increased considerably in brightness. A counter-clockwise rotation blackens the left side.

These phenomena prove that the planes of the disks in the flowing bentonite sol are arranged so that they lie tangent to the surfaces of cones whose apexes (of half-angle 12°) point in the direction of flow.

The angle of 12° did not seem to vary appreciably with the rate of flow. In fact, with the 2 per cent sol, the effect persisted indefinitely after the flow had stopped entirely. However, a noticeable increase in brightness appeared instantly if flow was allowed to start again. The intensity of the light became much less when the concentration of the sol was reduced, but even at 0.8 per cent the effect could still be observed and the angle was still about 12°.

A similar effect was observed with the tube (8 mm inside diameter) of 1.4 per cent bentonite sol (which had been used to study the temperature coefficient of τ) when this tube was placed vertically in ice water after having been made isotropic by immersion in water at 40°. After 20 to 60 seconds, examination between crossed Polaroids at 0° and 90° showed two broad side bands; the *left* one became black when the Polaroids were rotated 25° in a clock-

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wise direction. This indicated that the disks lay on a 25° cone with apex up. The effect gradually died away after a few minutes. After the sol had become isotropic at 0°C, immersion in the 40°C bath caused the side bands to reappear, but now the apex of the cone pointed downward.

These effects are due to vertical convection currents set up within the tube when its temperature is changed. Thus, when the tube is placed in ice water there is a thin layer of descending liquid close to the walls and a central upward return flow.

The direction of inclination of the bentonite disks with respect to the plane of shear is in every case that which we might expect by the following hypothesis. Take two neighboring points in the liquid which initially lie on a normal

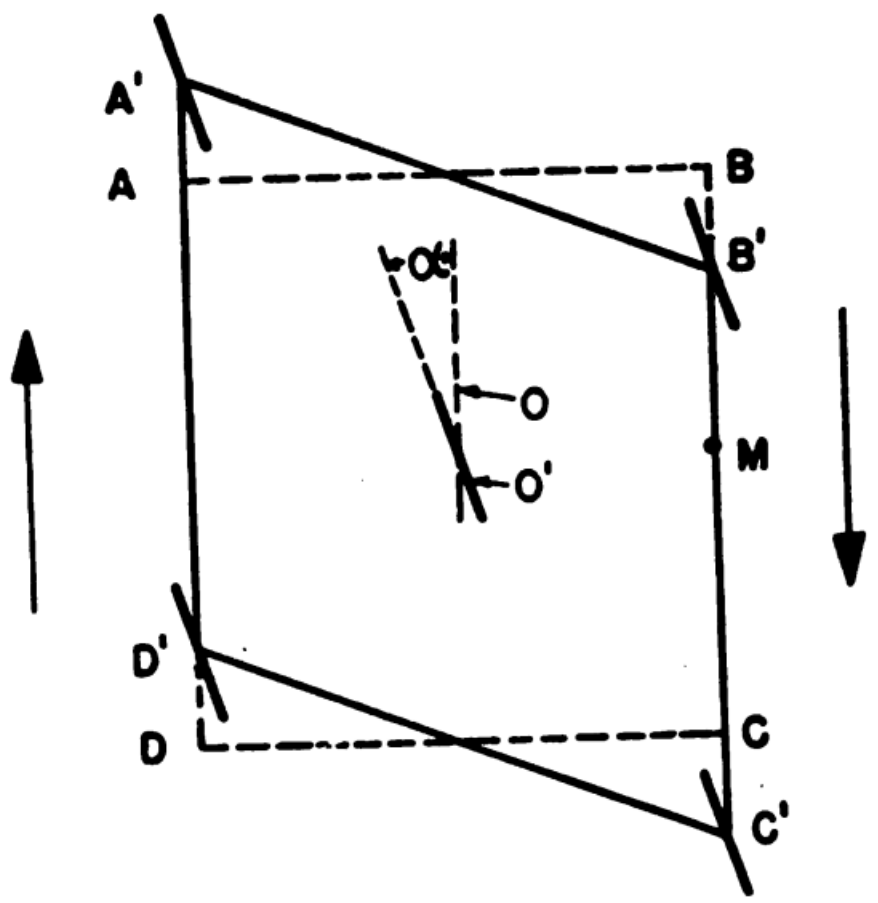

FIG. 1. Orientation of micelles due to shear.

to the plane of shear. The vector or line connecting these points sweeps through two opposite quadrants of a plane which is perpendicular to the plane of shear and parallel to the direction of shear. We find that the plane of the bentonite particles is perpendicular to the plane containing the vector, and the line of intersection of these two planes, which we may call the line of inclination, lies within the quadrants swept through by the vector and makes an angle α with the line of shear (same angle with plane of shear).

The probable mechanism of the tilting of the disks can be illustrated by Fig. 1. The square $ABCD$ represents the cross section through the center of a cube which has a micelle at the center O and one at the midpoint of each edge. If the liquid is subjected to shear, as shown by the arrows, the square $ABCD$ is changed into the parallelogram $A'B'C'D'$. Since the micelles at B' and D' are brought closer to the micelle at the center O, the repulsive forces between them are increased. Thus the micelle at O becomes inclined through

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an angle α, as shown by O'. If the points B' and C' move downward with uniform velocity while A' and D' move upward, α should pass through a maximum and fall to zero when B' reaches M, a point midway between B and C. During the rest of the travel while B moves from M to C, α will be negative. Thus the average value of α should be zero.

However, because of the repulsive forces between the particles, B' will not move with uniform velocity, but will take longer to travel from B to M than from M to C, since it slips through the surrounding liquid in accord with Stokes law. The average angle α will thus be inclined in the direction shown by O' in the figure. A further development of this theory should make it possible to calculate the viscosity of bentonite sols in terms of the distance between the particles and the charges on the particle. We plan to obtain experimental data by which to test these theories.

Let us now consider the optical effects that occur when the tube containing the bentonite sol is dipped into ice water. We should expect that in a layer extending from the wall of the tube to the cylindrical surface where the downward velocity is a maximum, the bentonite particles should be tilted so that their planes intersect the axis below the particle (cone apex downward). Between this surface of maximum downward velocity and the axis of the tube, the planes of the disks should intersect the axis above the level of the particle (cone apex up). In repeating the experiments with the tube plunged into ice water, careful examination between crossed Polaroids showed the presence of very narrow bands near the walls where the particles have the opposite inclination nearer the axis.

The lack of parallelism between the axes of rod-shaped micelles and the direction of shear has been studied in detail for V_2O_5 sols by Freundlich, Zocher[12-14] and others.

A "cross of isocline",[5] (Wirbelkreuz) was observed when the sol was placed between coaxial cylinders, one of which rotated, and was examined between crossed Nicols in a direction parallel to the axis. This cross was displaced with respect to the planes of polarization by an angle, which Edsall calls the angle of isocline: This is the complement of the angle α which we have used to measure the inclination of the particles to the direction of shear.

The data show that the angle α is close to zero with old V_2O_5 sols. New sols give angles up to 45°, which decrease at high rates of shear but are nearly independent of concentration.

The differences which we observed between the values of α for the bentonite flowing in the pipette (12°) and for the tube in which temperature

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[12] H. Freundlich, F. Stapelfeldt and H. Zocher, *Zeits. f. physik. Chemie* **114**, 190 (1924).

[13] H. Freundlich, H. Neukircher and H. Zocher, *Kolloid Zeits.* **38**, 43, 48 (1926).

[14] H. Zocher, *Kolloid Zeits.* **37**, 336 (1925).

[15] J. T. Edsall, *J. Biol. Chem.* **89**, 315 (1930).

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changes produced convection currents (25°) are undoubtedly due to this dependence of α on the rate of shear.

All the studies of bentonite which have been discussed so far were made with a sample of bentonite sol prepared in July, 1938. Recently Dr. Norton, in Schenectady, has prepared another monodisperse sol from white California bentonite in distilled water. The effective spherical diameter of the particles is approximately the same, 300A, as was found for the sol made previously. However, this new sample shows gel-like properties at considerably lower concentrations. Using sols ranging from 0.80 to 1.20 per cent, we have measured the times of disappearance of the birefringence at 0°, 20°, and 40°. A summary of the data obtained is given in Table I.

The three values τ_0, τ_{20} and τ_{40} for a given concentration were plotted on semilogarithmic paper against $1/T$ and straight lines were drawn which best

TABLE I

Time, τ, for Disappearance of Birefringence in Bentonite Sols at 20°C *and the Temperature Coefficient of τ from Measurements at* 0° *and* 40°C

Concentration per cent	τ_{20} sec	τ_0/τ_{40}	V volts	V calc. volts	τ calc. sec
0.80	—	—	—	0.042	1.5
0.920	4.2	—	—	0.068	4.6
0.968	8.	4.25	0.082	0.082	8.
1.065	31.	5.1	.116	0.114	28.
1.112	59.	5.6	.133	0.134	62.
1.137	260.	—	—	0.144	96.
1.160	>1000.	—	—	0.156	145.

represented these points. The value of τ at 20°C and the ratio τ_0/τ_{40} obtained from each of these lines are given in the 2nd and 3rd columns of Table I. By Eq. (2) the energy barrier V was calculated as given in the 4th column. Plotting these values of V against the concentration on double logarithmic paper a straight line was obtained whose slope was -3.46. Three times this, or 10.4, should correspond to the value of ϱ in Eq. (3).

When the values of log τ from the data in the 2nd column in the table were plotted against log n a straight line was obtained having a slope 14.3. The mean value of V over the range from 0.97 to 1.11 per cent is 0.104 volt. Substituting these values into Eq. (4), we obtain $\varrho = 10.5$, in agreement with the value of ϱ from the temperature coefficient.

Using $\varrho = 10.5$ in Eq. (3) we calculate V as given in the 5th column of Table I. These values agree well with those calculated from the temperature coefficients. Substituting these values of V into Eq. (2) and choosing a single appropriate value of A, we obtain τ as given in the 6th column. Up to a concen-

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tration of 1.11 per cent the agreement with the experimental data of the 2nd column is excellent, but at higher concentrations the observed values of τ increase much more rapidly than those calculated. In fact, at 1.16 per cent permanent birefringence already sets in.

Dr. Norton finds that with this sol in concentrations from 1.2 to 1.5 per cent, a sharply defined polycrystalline phase separates out in about 24 hours of quiet standing or after only 10 minutes of centrifuging. The bounding line is a sharp horizontal plane, and if the tube (6 mm diameter) is tilted, the boundary moves with the tube, but after several minutes in the tilted position the crystalline phase flows sufficiently to bring the boundary nearly back to a nearly horizontal plane. Analysis of the top and bottom phases in one of the tubes gave 1.16 and 1.35 per cent, respectively.

A tube 2 cm diameter, 15 cm long was half-filled with a series of bentonite sols of decreasing concentrations. Birefringence could be observed on tilting the tube to a horizontal position even at concentrations as low as 0.05 per cent.

Comparing these data with those given by the first bentonite sample, we note that the value of ϱ is only a little more than half as great as the value 20 previously found; the concentration at which $V = 0.080$ volt is now about 1.0 per cent, whereas formerly it was 1.5 per cent, and the lowest concentration at which separation into phases occurs is 1.2 instead of 2.0 per cent.

The data of Table I indicate that the theory which led to Eqs. (2) and (4) is quite accurately applicable to these bentonite sols, so that the exponent ϱ should be an important characteristic of sols of this type. The variations in ϱ may be due to changes in the average shape of the micelles, the lower value presumably corresponding to more elongated particles.

We intend to make further studies of these bentonite sols determining the dependence of ϱ on the presence of low concentrations of salts and on particle size.

Vanadium Pentoxide Sols

The bentonite sols whose properties we have investigated constitute perhaps the most striking example of sols containing disk-shaped particles.

For comparison we have studied vanadium pentoxide sols which have rod-shaped particles. We have used a sol, containing 2.0 per cent of V_2O_5 in distilled water, which was made up 17 years ago. This was diluted with distilled water to give a series of solutions of different concentrations. When these were allowed to flow through the tube of a pipette (8 mm inside diameter) and examined between crossed Polaroids, birefringence was observed which persisted for several seconds after the flow was stopped, even at a concentration as low 0.002 per cent V_2O_5.

With increasing concentration, the time τ required for the disappearance fo the birefringence after stopping the flow increased with the 1.8th power

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of the concentration at concentrations in the neighborhood of 0.015 per cent, and still more rapidly at concentrations of 0.02 per cent. At 0.015 per cent τ was 120 seconds. This increase with the 1.8th power of the concentration may be compared to the corresponding exponents 22.4 and 14.3 which we observed with the bentonite sols.

With solutions of concentrations of 0.010, 0.015, and 0.020 per cent we measured the temperature coefficient of τ between 0° and 40°C. The temperature coefficient increased with increasing concentration: Thus the ratios τ_0/τ_{40} were 2.9, 3.5 and 4.1, at the concentrations of 0.010, 0.015 and 0.020 respectively. Allowing for the temperature coefficient of η in accordance with Eq. (2), we find that V is negligibly small at 0.01 per cent and increases to 0.046 volt at 0.015 per cent and to 0.089 volt at 0.020 per cent. Applying Eqs. (3) and (4), as for the bentonite, we find the best fit with the data is obtained when we choose $\varrho = 4$ for V_2O_5 sols as compared to $\varrho = 20$ and $\varrho = 10.5$ for the two bentonite sols. The experimental data, however, do not agree with the equations as well as in the case of bentonite, so that $\varrho = 4$ is a rough approximation.

There are at least two reasons why the equations are not so accurately applicable to the V_2O_5 sols. In the first place the sol had not been made monodisperse by centrifugation, and therefore contained particles having a wide range of sizes. Secondly, the mechanism by which the particles lose their orientation in the V_2O_5 sols is in many ways different from that which we have postulated for bentonite sols, so that the assumptions underlying Eq. (3) are not strictly applicable. Furthermore, the average distance between the particles, which are lined up in parallel directions in the anisotropic sol, does not necessarily vary in proportion to $n^{-1/3}$ as it does for bentonite, but may vary with $n^{-1/3}$ if the end-to-end distance between rod-shaped oriented particles is independent of concentration.

We can readily understand why the concentrations at which perceptible persistence of orientation is observable is so much lower with the V_2O_5 sols than it is with the bentonite. For the rod-like particles, with diameters very small compared to their lengths, the length of the rods will be greater than the lateral distances between them even at relatively great dilutions. With the more compact bentonite disks, however, the diameter of the disk becomes comparable with the distance between the particles only at very much higher concentrations.

Let us consider a V_2O_5 sol of parallel rodshaped particles of such concentration that the average lateral distance between the particles is a little less than the average length of the particles. If a single particle has its longitudinal axis turned through 90°, the ends of the particle are forced between pairs of adjacent parallel molecules. The potential energy resulting from the repulsion between the displaced molecule and its neighbors will depend upon the lateral distances between molecules. However, this energy will not vary with a high power of this distance. The problem is closely related to that of the potential energy of

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two charged cylinders of small diameter whose axes are separated by a distance r but are respectively parallel to two axes that are at right angles to one another. (90° skew angle). The value of ϱ corresponding to the variation of this potential with r should have a relatively low value.

At higher concentrations the displaced molecules are brought close to more than four other molecules. At very low concentrations, on the other hand, the lateral distance between molecules should be greater than the length of the rods, and therefore ϱ probably increases. Thus for V_2O_5 ϱ should not be constant over a wide range, as in the case of bentonite.

When the old V_2O_5 sol that we used flows through the tube of a pipette it acts as a uniaxial crystal. Thus it transmits no light between the crossed Polaroids when these are in the 0–90° position. When the Polaroids are turned to the 45° position, the transmitted light reaches a maximum but shows no trace of the central dark band which was observed with the bentonite sols, and which we attributed to the disk-like nature of the bentonite particle.

We must thus conclude that in this V_2O_5 sol, flowing with moderate velocity through a tube, the particles are completely oriented, parallel to the direction of flow so that $\alpha = 0°$. This agrees with previous conclusions[12] that α is close to zero for very old V_2O_5 sols in which the particles have great lengths. In such sols, as in tobacco virus solutions[2], there is probably no regularity of micelle arrangement in directions parallel to their length, so that the forces illustrated by Fig. 1 which cause the tilting are absent. In new V_2O_5 sols, however, the shorter particles permit a three-dimensional rather than a two-dimensional lattice arrangement and so give $\alpha \neq 0$.

Protein Crystals and Tactoids

Our observations with tobacco virus and bentonite lead us to believe that the separation of thixotropic gels into two phases on standing is a common phenomenon among sols which consist of highly charged particles or molecules. Bernal and Fankuchen[2] consider that Stanley's so-called needle-shaped crystals of tobacco mosaic virus protein are paracrystals, or sharply defined regions consisting of an anisotropic liquid phase. It seems preferable, however, to recognize the fact that they are tactoids, thus extending the definition of tactoid to include cases where the particles are large molecules.

There seems to be no advantage in regarding a tactoid as a type of liquid crystal; it appears to be essentially a solid crystal, often having such low mechanical strength that it appears to flow like a liquid. The lower phases that separate from a 2 to 3 per cent tobacco virus solution or a 1.2 to 2.0 per cent bentonite solution are built up of interlocking tactoids which from crystal grains giving a structure much like that observed with single-phase metallic alloys. The structure is permanent if undisturbed and Brownian movement is absent. Yet if the test tube containing the sol is tilted slightly, the phase boundary remains

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or soon becomes horizontal, showing the exceedingly low mechanical strength of this thixotropic gel.

Tactoids which are formed from more concentrated solutions (or by the addition of salts, as in the case of tobacco virus crystals) may have such high mechanical strength that they would normally be regarded as solids. Tobacco virus "crystals" have two characteristics which seem to distinguish them from most other crystals: (1) The distance between molecules increases continuously as the water content increases. (2) The molecules are not regularly spaced along a direction parallel to the long axes of the molecules.

The first of these characteristics seems to be a general property of protein crystals. Recent X-ray studies[16] of lactoglobulin, tobacco seed globulin, chymotrypsin and heamoglobin have shown that the volume of the unit crystallographic cell shrinks by 27 to 42 per cent when crystals of these proteins are dried in the air. This shrinkage is accompanied by a disordering of the structure, since the smallest observable x-ray spacings increase progressively from about 2A up to 20A.

The second characteristic of tobacco virus crystals (lack of order along optic axis) is not observed with the other protein crystals and appears to be caused by the unusually great length of the rod-shaped virus molecules.

The fact that a high but indefinite water content forms an essential part of protein crystals justifies us in regarding them all as tactoids. According to this concept, each protein molecule, which is surrounded by an envelope that may contain several thousand water molecules, is held in a position of equilibrium by repulsive forces resulting from charges on the molecule.

Coacervates

Bungenberg de Jong and his co-workers have published[17] a large number of papers in recent years dealing with the unmixing or coacervation of liquids into two phases. The most striking examples of this kind are furnished by colloidal solutions containing both positive and negative micelles. For example, if a dilute solution of gelatin (positive micelles) is mixed with a dilute solution of gum Arbaic (negative micelles), droplets of a liquid phase separate out. We shall call this bipolar coacervation.

Numerous other examples are given where a colloid having charged particles is coacervated by the addition of a salt containing polyvalent ions of opposite sign. For example, if a solution of strontium chloride is mixed with ammonium molybdate, a second liquid phase is formed. This we shall call unipolar coacervation.

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[16] D. Crowfoot, D. Riley, *Nature* **141**, 521 (1938); D. Crowfoot, I. Fankuchen, *ibid.* **141**, 522 (1938); J. D. Bernal, I. Fankuchen, M. Perutz, *ibid.* **141**, 523 (1938).

[17] H. G. Bungenberg de Jong, *Kolloid Zeits.* **79**, 223, 334 (1937); **80**, 221, 350 (1937). These articles give references to and a summary of about 30 previous papers.

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When ammonia gas is led into a strong solution of potassium or rubidium carbonate or tripotassium phosphate, a two-phase system is formed which has been studied in detail by Jänecke[18]. Undoubtedly these are also examples of coacervation (probably bipolar).

Another interesting unipolar coacervate has been called to my attention by Dr. E. P. Partridge. When a strong solution of sodium hexametaphosphate is mixed with a strong solution of calcium chloride, the liquid separates into two isotropic layers, the lower being a very viscous liquid. In this case the negative ions are undoubtedly of very high molecular weight, while the positive ions are sodium ions.

The separations of tobacco virus and of bentonite sols into two phases seem to be typical examples of unipolar coacervation. On this basis we should also look upon tactoids as coacervates. Protein crystals are merely solid coacervates.

Bungenberg de Jong has classified various types of coacervation and has given a "working hypothesis" for the mechanism of their formation. In the case of "complex coacervates", which we call bipolar, the attractive forces between the positive and negative colloidal particles can account for their gathering together in a separate phase. However, since these coacervates usually contain 80 to 90 per cent water and are liquid, it is necessary that there should be some repulsive force that prevents the positive and negative particles from coming into contact. The hypothesis is made that the intense electric field draws the dipole water molecules into the spaces between the particles and so holds them apart. The theories of Bungenberg de Jong are not so satisfactory when applied to the unipolar coacervates such as strontium, molybdate, calcium hexametaphosphate, tobacco virus and bentonite.

Attractive and Repulsive Forces in Unipolar Coacervates

We have seen from our consideration of the bentonite sols that large negatively charged colloidal particles, because of the repulsive force they exert upon one another, tend to become arranged in a definite crystal lattice. These forces can cause elasticity and anisotropy of thixotropic gels and tactoids and the disappearance of the Brownian movement. However, the spontaneous gathering together of particles into tactoids or into birefringent liquid phases indicates the presence of long range *attractive* forces, which under some conditions can outweigh the effect of repulsive forces.

Kallmann and Willstätter[19] assumed that van der Waals attractive forces between colloidal particles might be of sufficient range and intensity to account for the formation of tactoids.

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[18] E. Jänecke, *Zeits. f. Elektrochemie* **33**, 518 (1927).

[19] H. Kallmann and M. Willstätter, *Naturwiss.* **20**, 952 (1932).

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This idea has been accepted by Freundlich[20] and has been developed quantitatively,[21,22] and applied to colloid systems[23] by H. C. Hamaker. He calculates that the potential of the van der Waals attraction between two thick flat plates separated by the distance d should vary with d^{-2}. In the case of equal spheres he finds that the potential energy is of the order of kT when the distance between the surfaces of the spheres is 0.1 to 0.5 of their diameter. These calculations, however, are based on the very improbable assumption that these forces involve a kind of "action at a distance" and are not influenced by the medium through which they are transmitted.

Hamaker analyzes the characteristic properties of colloids by means of diagrams in which the potential energy of the forces acting between two colloid particles is given as a function of the distance between them. He then regards this total potential as resulting from the superposition of the potentials of attractive and of repulsive forces. He believes[24] that the repulsion is due to the electric charges on the particles in accord with the Debye-Hückel theory, while the attraction is the result of van der Waals forces and is independent of the charge or the ion content of the solution. Adding the two potentials, he shows that a minimum potential may occur when the particles are at distances of the order of 1000A.

Houwink[25,26] makes a similar analysis of the repulsive electrostatic forces and the attractive van der Waals forces to explain the properties of colloids and in particular the yield value.

In a recent paper Bergmann, Löw-Beer and Zocher[27] have calculated the repulsive forces due to the charges between Schiller layers of tungstic oxide sols and have equated these to the gravitational force. To obtain the repulsion they used a modification of the Gouy-Debye-Hückel theory. They considered only experimental data in which separate phases do not appear. They make the statement that electrostatic forces cannot explain the attractive forces in gels having micelles which all have similar charges.

The authors of these theories of colloidal structure recognize the repulsive forces between micelles of like charges and take it as axiomatic that this charge must be balanced by a long range attractive force which is not of electrostatic

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[20] H. Freundlich, *Thixotropy* (Paris, 1935).

[21] H. C. Hamaker, *Physica* **4**, 1058 (1937).

[22] H. C. Hamaker, *Recueil des Travaux Chimiques des Pay-Bas* **57**, 61 (1938).

[23] H. C. Hamaker, *Recueil des Travaux Chimiques des Pay-Bas* **56**, 727 (1937).

[24] H. C. Hamaker, *Recueil des Travaux Chimiques des Pay-Bas* **56**, 1 (1937).

[25] R. Houwink and W. G. Burgers, *Elasticity, Plasticity and Structure of Matter* (Cambridge University Press, 1937). See especially pp. 338–343.

[26] *Second Report on Viscosity and Plasticity* (Committee of the Academy of Sciences at Amsterdam) (Nordermann Publishing Company, N. Y., 1938). See pp. 233–237, of Chapter 4 by R. Houwink.

[27] P. Bergmann, P. Löw-Beer and H. Zocher, *Zeits. f. physik. Chemie* **181A**, 301 (1938).

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origin. They agree that the only conceivable attractive force that will meet their needs is the van der Waals force.

It will be shown in the following pages that there are at least three fundamental fallacies involved in this use of energy diagrams to analyze the stability of colloids.

(A) No direct account is taken of the thermal agitation which by itself would tend to cause the colloid particles and the ions to be dispersed throughout the liquid giving an osmotic pressure $p = \sum nkT$.

(B) The attraction between the charged micelles and the ion atmosphere of opposite sign which extends throughout the intervening liquid is ignored or neglected although it exceeds the repulsive force between the micelles.

(C) The electric charges on the micelles are assumed to be constant, whereas they must be, in general, dependent on the concentration of the micelles.

Let us analyze the general problem of the forces and energies responsible for the stability of colloids. We will first consider a colloidal solution having large positive micelles of charge z_1e, while the equivalent opposite charge is distributed throughout the intermicellar liquid in the form of negative ions of charge $-z_2e$. Let this solution be confined by a piston which is permeable to water but impermeable to both the micelles and to the ions. On the other side of the piston we assume there is pure water.

If the forces due to the interaction of the charges could be neglected, the pressure on the piston (Factor A) would be

$$p = (n_1+n_2)kT, \tag{5}$$

where n_1 and n_2 are the concentrations of the micelles and of the ions, respectively. Since the total charge must be zero, we have

$$n_1z_1 = n_2z_2 \tag{6}$$

and thus Eq. (5) becomes

$$p = (1+z_1/z_2)n_1kT. \tag{7}$$

This force which is due merely to thermal agitation or Brownian movement is not a repulsive force between particles and so is not explicitly considered in a theory such as Hamaker's which is based on potential energy diagrams.

The second factor (B), which takes into account the effect of the electric charges, can be illustrated by considering a sodium chloride crystal. The distance between any ion in this lattice and its oppositely charged neighbor is less than the distance between the ion and its nearest neighbor of like sign. The attractive forces between unlike ions thus exceed the repulsive forces between like ions so that the crystal lattice should tend to shrink.

From simple dimensional considerations it is obvious that the effect of the Coulomb forces alone is to reduce the size of the lattice. Thus a crystal lattice built up of positive and negative point charges (z_1e and $-z_2e$, respectively) has an energy per ion (of any given type) equal to

$$E = -\varkappa z_1z_2e^2/a, \tag{8}$$

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where $\varkappa$ is a constant depending upon the type of lattice, and a is the lattice constant. From this it follows that as a decreases, the energy decreases without limit so that stable equilibrium can occur only if some *repulsive force* other than the Coulomb interaction is called into play.

Exactly the same consideration must apply to a colloidal solution (unipolar) which has micelles of one sign with small ions of the opposite sign distributed within the intermicellar liquid. The interaction of these charges, just as in the sodium chloride crystal, gives an excess of attractive force and in order to have equilibrium it will be necessary not to have an additional *attractive* force, such as the van der Waals force postulated by Hamaker, but some new kind of *repulsive* force.

It is natural, therefore, that as the concentration increases, the effect of the attractive forces should exceed the dispersing tendency of the Brownian movement and tend to cause the colloid to draw together into a more condensed phase (unipolar coacervate). If no other repulsive force than that which acts between particles in contact were involved we should expect the colloid to form a dense precipitated solid mass from which the water has largely been expelled. Of course, this is just what happens when the concentration of a sodium chloride or other salt solution is increased too much; the salt crystallizes out in an anhydrous form or with a small amount of water of crystallization.

To account for the existence of unipolar coacervates which contain large amounts of water, we must either find some long range repulsive force or we must be able to show that the electrostatic attractive force is such a function of the distance between particles that a state of equilibrium can be reached (Factor C).

Equation (8), from which we concluded that the electrostatic force would tend to cause the separation of a dense phase, was based on the assumption that the charges on the particles remain constant when the distance between the particles is varied. Now in the case of colloidal particles it is probable that the charge on the micelles decreases as the concentration of the colloid increases. From the viewpoint of Eq. (8), therefore, we can see that if $z_1 z_2$ decreases faster than a decreases, the potential energy will rise at increasing concentrations so that there may be a definite concentration which gives a stable second phase.

A complete theory of the interaction of micelles with ionic atmospheres covering the whole range of concentrations would present insuperable mathematical difficulties. However, a very concentrated colloid phase in equilibrium with a dilute phase can be treated by an elementary consideration of two simple limiting cases.

In the theory of the potential distribution in the neighborhood of tungsten filaments in caesium vapor, which I have considered elsewhere[28], there are many features which are fundamentally related to those of colloids. A tungsten

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[28] I. Langmuir, *Phys. Rev.* **43**, 224 (1933).

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filament in equilibrium with a given pressure of caesium has a definite electron emission and positive ion emission at a given temperature. In the interior of the caesium vapor at a large distance from the tungsten surface there are equal concentrations, n_0, of caesium ions and electrons, so there is no space charge. Taking the potential of this plasma to be zero, the potential of the tungsten filament is a function only of its temperature and of the caesium vapor pressure. It does not depend upon the size or shape of the tungsten surface. One could, for example, have fine tungsten particles distributed in any manner through the space and the potential of every surface would be the same. This corresponds then to the ζ-potential of colloidal particles. Abramson[29] has shown that the ζ-potential of quartz particles on which a given protein is adsorbed is independent of the size or shape of these particles.

Now let us consider that we bring some of the tungsten particles (or micelles in a colloid) so close together that their ionic atmospheres overlap. Since the ζ-potentials remain constant, it is necessary that the charges on the particles shall decrease.

Take, for example, a two-phase colloidal system in which a semi-permeable membrane, to which pressure can be applied, separates the two phases. Let the membrane be permeable to electrolytic ions but impermeable to the micelles of the colloid. In the dilute phase at sufficiently large distances from the micelle, the concentrations of positive and negative ions, both assumed univalent, will each be equal to n_0.

If the micelles are positively charged and have a potential V_1 (the ζ-potential), the concentration of negative univalent ions very close to the surfaces of the micelles is given by the Boltzmann equation

$$n_n = n_0 \exp(V_1 e/kT) = n_0 \exp \eta_1, \tag{9}$$

where for convenience we have put

$$\eta = Ve/kT = 11{,}600V/T, \tag{10}$$

if V is expressed in volts. Similarly the concentration of positive univalent ions is

$$n_p = n_0 \exp(-V_1 e/kT) = n_0 \exp(-\eta_1). \tag{11}$$

In the ordinary approximate form of the Debye-Hückel theory η is assumed to be numerically small compared to unity. We wish, however, to consider colloids which have highly charged micelles, for these are the ones which show the separation into two phases (unipolar coacervation). For such colloids $n_1 \gg 1$, since the ζ-potential is far greater than the value 0.025 volt which corresponds to kT at room temperature according to Eq. (10). Close to the surface of a positive micelle, in a region where $\eta > 2$, the concentration of positive ions, by Eqs. (9) and (10), is negligible compared to that of the negative ions, so that there is a sheath of firmly bound negative ions surrounding the positive micelle.

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[29] H. A. Abramson, *Electrokinetic Phenomena* (Chemical Catalog Co., New York, 1934). See especially pp. 111–114.

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At larger distances, where the potential is less than about 0.04 volt, positive as well as negative ions are present and the conditions postulated in the Debye-Hückel theory are fulfilled. It thus appears that the properties of the dilute phase can be treated by the Debye-Hückel theory if one replaces the micelle with its large positive charge by a point charge having an appropriate fictitious charge. This effective charge is roughly equal to the charge on a micelle reduced by the firmly bound negative ions in the sheath.

Fuoss[30] has shown that ion association of this kind plays an important part in the theory of the properties of electrolytes in solvents of low dielectric constant. It also becomes important in solvents of high dielectric constant such as water, if one of the ions has a charge high enough to give a potential above about 0.07 volt.

Let us now examine the conditions that exist within the concentrated phase which is in equilibrium with the dilute phase. Since the potential V_1 of the particles in this phase must be the same as that of similar particles in the dilute phase, we see that the limiting concentration n_1 of negative ions close to the surface of the particles has the same value as for the particles in the dilute phase.

If the particles in the concentrated phase are brought very close together, the charge carried by the solvate between the micelles, since n_n cannot exceed n_1, must decrease about in proportion to the volume of this solvate included in this denser phase, and there must be a similar decrease in the positive charge on the micelles. When the concentration of the micelles becomes very high, the whole phase tends to acquire a nearly uniform potential throughout, close to V_1, and the charges on the particles and in the solvate become very small. At the phase boundary, however, there is sharp drop in potential so that, according to the Poisson equation, there must be an electric double layer. In the denser phase the electric forces may become negligible in determining the pressure p which would then be given by

$$p_1 = n_1 kT = n_0 kT \exp (V_1 e/kT). \tag{12}$$

This theory then enables us to calculate a limiting pressure which can exist within the condensed phase as the concentration increases.

If desired, this pressure can be described as a repulsive force existing within the concentrated phase. It has the characteristics of the repulsive force that we have found necessary to counteract the excess of electrostatic attractive forces within the colloid.

At somewhat lower concentrations of the colloid than those we have just considered, the potential V in the intermicellar spaces will range between V_1 at the surface of the micelles to some lower minimum value V_M at points in the liquid which are farthest from the micelles. The pressure within the concentrated phase will then have some value intermediate between p_1 and p_M

[30] R. M. Fuoss, *Trans. Faraday Soc.* **30**, 967 (1934); *Chem. Revs.* **17**, 27 (1935).

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where p_M can be calculated from Eq. (12) by replacing V_1 by V_M. As the micelle concentration decreases the charge on the micelles increases, and an increasingly large role is played by the electrostatic forces.

The Debye-Hückel Theory (1st Approximation) Applied to the Dilute Phase

The approximate conditions required for the appearance of two phases can be derived from the Debye-Hückel theory of osmotic pressures[31]. A calculation of this kind has already been made[32] for the case of highly ionized caesium vapor at high pressures. The equations that were developed, modified by the introduction of the dielectric constant and the unequal charges on positive and negative ions, are applicable to colloidal solutions.

The osmotic pressure p in an electrolytic solution according to the 1st-order approximation given by Debye and Hückel is

$$p = kT \sum n_i - e^2 \sum (n_i z_i^2)/6D\lambda, \tag{13}$$

where λ, which we may call the Debye distance, is

$$\lambda = [DkT/4\pi e^2 \sum (n_i z_i^2)]^{1/2}. \tag{14}$$

Elimination of λ between these two equations gives

$$p = kT \sum n_i - (\tfrac{1}{3}) (\pi e^6/D^3 kT)^{1/2} [\sum (n_i z_i^2)]^{3/2}. \tag{15}$$

The first term in the second member of this equation represents the pressure of all the ions, according to the ideal gas law, as if there were no electric forces. The second term gives the (1st-order) effect of the electric charges. It should be noted that the sign of this term is always negative, indicating that the effec of the interaction of the charges is equivalent to a net electric attraction and not a repulsion as was assumed in the theories of colloid structure that have been cited.

We have previously derived Eqs. (5), (6) and (7) for the effect of Factor A (thermal agitation) in the case of large positive ions of charge $z_1 e$ and concentration n_1 with small negative ions of charge $-z_2 e$ and concentration n_2. We can now apply Eq. (15) to modify these equations to take into account Factor B (electric interaction). Eliminating n_2 from Eq. (15) by means of Eq. (6), we obtain in place of Eq. (7)

$$p = (1 + z_1/z_2) n_1 kT - (\tfrac{1}{3}) (\pi e^6 D^3 kT)^{1/2} z_1^{3/2} (z_1 + z_2)^{3/2} n_1^{3/2}. \tag{16}$$

By choosing appropriate units for p and n_1 this equation can be written in the simple form

$$p = 3n - 2n^{3/2}, \tag{17}$$

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[31] P. Debye and E. Hückel, *Physik. Zeits.* **25**, 97 (1924).

[32] Reference 28, p. 226.

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for which a plot is given by the curve *OBCG* in Fig. 2. The maximum, found from Eq. (17) by placing $dp/dn = 0$, is located at $n = 1$, $p = 1$. In a similar way the maximum value of p according to Eq. (16) occurs when

$$n_1 = 4(DkT)^3/\pi^6 z_1^3 z_2^2 (z_1+z_2) \tag{18}$$

and

$$p_M = 4kT(DkT)^3/3\pi e^6 z_1^3 z_2^3. \tag{19}$$

The straight line *OA* in Fig. 2 corresponds to the ideal gas law (Factor *A*) and the deviations of the curve *OBC* from this line are due to the electric effects (Factor *B*).

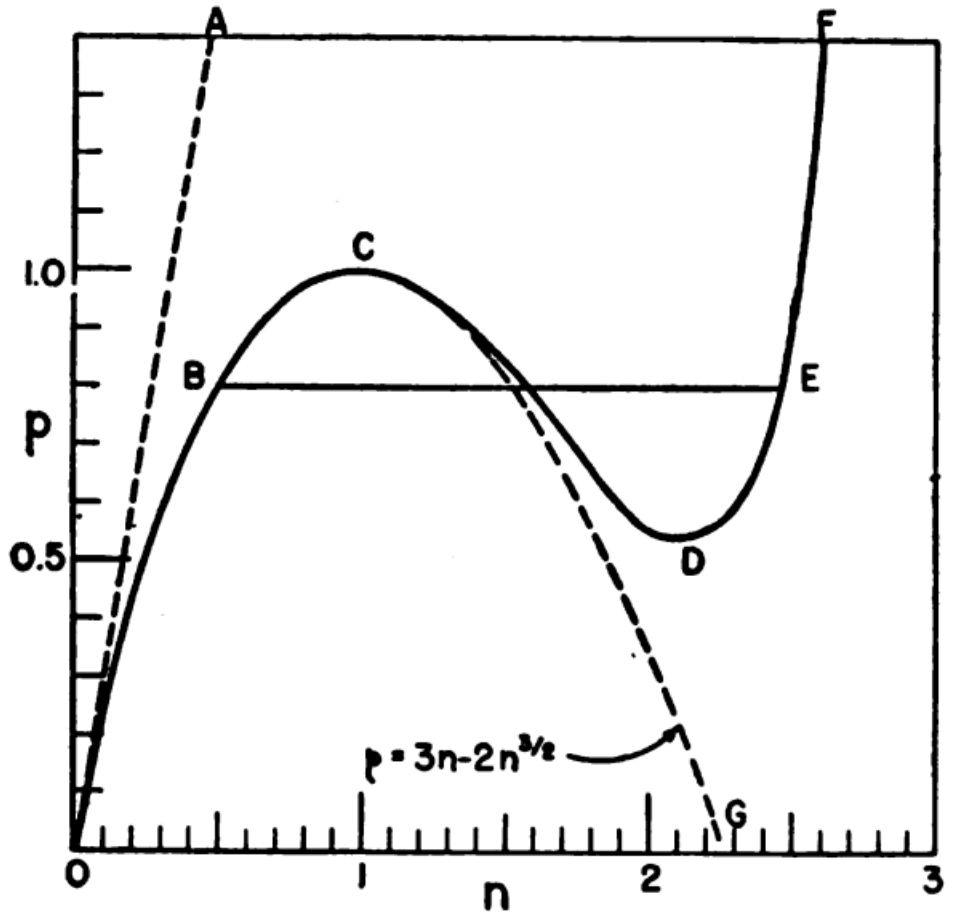

FIG. 2. Pressure-concentration curve illustrating conditions for coacervation.

If p reaches a maximum at one value of n_1 it is certain that at still higher values of n_1 it must have a minimum value, since p must rise to very high values when the particles come into contact. Thus, if there is a maximum in p, the curve must have some such shape as *OBCDEF*. The location of the portion *DEF* will be determined by repulsive forces between particles or by (Factor *C*) a decrease in z_1 at high values of n_1. We shall give further consideration to *DEF* in a later section.

The portion *CD* of the curve between the maximum and minimum values of p is a region of instability, just as in the van der Waals theory of the continuous transition between the liquid and gaseous states. Therefore, whenever a maximum occurs we have conditions which necessarily cause two phases to appear as indicated by the points *B* and *E* with the horizontal line connecting them. The exact location of both *B* and *E* must depend upon the shape of the whole intermediate part of the curve *BCDE*. The theory of the *CD* portion must present almost insuperable mathematical obstacles, but the theories of the two limiting cases corresponding to the portions *OBC* and *DEF*

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are far simpler and can probably be developed without great difficulty. Eq. (16) is a first approximation to such a theory for the portion *OBC*.

In the case of many colloids, Factor C, which has an effect like that of a repulsive force of the type illustrated by Eq. (12), may come into play before the concentration has reached the value given by Eq. (18), and this may prevent the occurrence of the maximum in p. The curve then shows a point of inflection while the slope is still positive. This corresponds to a liquid-gas system above its critical temperature. Under these conditions two phases will not occur until such high concentrations are reached that repulsive forces due to contact come into play.

Let us consider an aqueous solution ($D = 81$, $T = 293°K$) containing w grams per ml. of a substance, of molecular weight M, whose molecules dissociate into one positive ion of charge $z_1 e$ and z_1/z_2 negative ions each having a charge $-z_2 e$. Then Eq. (18) takes the form

$$w_M = 6.15 \times 10^{-3} M/z_1^3 z_2^2 (z_1 + z_2). \tag{20}$$

Here w_M is the value of w that corresponds to the maximum at C in Fig. 2.

Table II gives data calculated by Eq. (20) for a few typical salt solutions and colloids. In the first three examples w_M has been calculated from the known values of z_1 and z_2. The fact that these values of w_M are of the same order of magnitude as the solubilities of common inorganic salts illustrates the importance of the factors which we have considered in the derivation of this theory. There are several reasons why exact values for the solubility cannot be given by Eq. (20). The true equilibrium point B in Fig. 2 corresponds to a concentration which is necessarily lower than at the point C in the curve by an amount that depends upon the whole curve *BCDE*. Thus if the condensed phase at E is of unusually high stability (for example $BaSO_0$) the solu-

TABLE II

The Concentrations, w_M, in g per ml. which Give a Maximum Osmotic Pressure for Solutions of Various Types. Based on Eq. (20).

Example	Solution	M	z_1	z_2	w_M	c ($z_3 = z_0 = 1$)
1	NaCl	58	1	1	0.180	3.1 molar
2	$BaCl_2$	208	2	1	0.053	0.8
3	$MgSO_4$	120	2	2	0.006	0.19
4	Protein	35,000	4	1	0.67	0.19
	,,	,,	6	1	0.14	0.085
	,,	,,	6	2	0.031	—
5	Tobacco virus	5×10^7	53	1	0.04	0.0011
6	Bentonite	10^9	133	1	0.02	2×10^{-4}
7	Spheres 1μ diameter	6×10^{11}	660	1	0.020	—
	,,	,,	660	2	0.005	—

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bility may be far less than given by Eq. (20). On the other hand, hydration of the ions, as illustrated by the water of crystallization in $MgSO_4 7H_2O$, may increase the solubility above w_M. Of course, we must consider also that the Debye-Hückel theory on which Eq. (20) is based cannot be expected to apply accurately to solutions as concentrated as those in the first three examples.

A protein of molecular weight of 35,000 has been chosen for Example 4. It was assumed that the protein gives micelles of charge z_1 and univalent ions, $z_2 = 1$, in solution. With $z_1 = 4$ or 6 we obtain values of w_M of 0.65 or 0.14, respectively. Thus the theory indicates that proteins of this molecular weight could be highly soluble in water if they have charges on the micelles which do not exceed about 6. If very low concentrations of divalent ions, $z_2 = 2$, are present the solubility would decrease to about one-quarter. It is known[33] that proteins such as egg albumin have values of z_2 that are positive when the pH of the solution is below the isoelectric point and negative for values of pH above the isoelectric point. The rate of change of the charge is about 8 units for each unit of pH. Thus, the value $z_2 = 6$ corresponds to pH values which differ from the isoelectric point by about 0.8 unit. It is seen that the effect of low salt concentrations as calculated by Eq. (20) is in general accord with the Schulze-Hardy rule.

In Example 5 with tobacco virus having a molecular weight of 50,000,000, we choose for w_M a value twice that at which coacervation was observed. We then calculate $z_1 = 53$. Of course, Eq. (20) cannot hold accurately in this case for it was based on the assumption of spherical molecules, and it is known that tobacco virus molecules are long rods. However, the order of magnitude of the calculated value of z_1 seems reasonable.

The molecular weight of bentonite sols is of the order of 10^9, and if we again take for w_M twice the concentration (1 per cent) needed for coacervation we calculate $z_1 = 133$.

The last example is that of a colloidal solution of spheres 10^{-4} cm in diameter, of density 2, and therefore molecular weight 6×10^{11}. Here to get coacervation in a 1 per cent solution a charge $z_1 = 660$ is required. The presence of divalent ions of the opposite polarity would give coacervation at a concentration only one-quarter as great.

The Effect of Added Salts

Besides the ions of charge $z_1 e$ and $-z_2 e$, let us assume that we have also a concentration of some salt, giving per unit volume n_3 positive ions with a charge $z_3 e$ and n_4 negative ions with a charge $-z_4 e$. Then in addition to Eq. (6) we have the condition

$$n_3 z_3 = n_1 z_4 . \tag{21}$$

[33] L. S. Moyer and J. C. Abels, *J. Biol. Chem.* **21**, 331 (1937).

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Substitution of these values into Eq. (15) gives an expression for p in terms of n_1 and n_3. If we take the partial derivative of p with respect to n_1 and equate this to zero, we obtain an equation which enables us to calculate roughly the concentration of protein or of salt which will correspond to the maximum C in Fig. 2. This equation is

$$n_1 z_1(z_1+z_2)+n_3 z_3(z_3+z_4) = 4(DkT)^3/\pi e^6 z_1^2 z_2^2 = 2.79\times 10^8 D^3T^3/z_1^2 z_2^2. \quad (22)$$

An increase in the amount of added salt thus decreases the colloid concentration at which p becomes a maximum. The concentration c, in mols per liter, needed to reduce n_1 to zero, is given by

$$c = 6.15/z_1^2 z_2^2 z_3(z_3+z_4). \quad (23)$$

The last column of Table II gives values of c calculated from Eq. (23) assuming that the ions of the added salt are univalent ($z_3 = z_4 = 1$). Concentrations only one-quarter as great of a di-di-valent salt would be needed. This would indicate that ordinary proteins are sensitive to salts in 100 to 200 millimolar concentrations, while bentonite sols, in accord with observations, are affected in their coacervation properties by far lower concentrations.

Debye-Hückel 2nd Approximation. Effect of Particle Size

The approximate form of the Debye-Hückel theory that we have used has shown that electrostatic forces result in a net attraction that can account at least qualitatively for unipolar coacervation.

Debye and Hückel, in a kind of second approximation, have considered the effects of the finite sizes of the ions. Their expression for the osmotic pressure[34] in the case where the charge and diameter of the micelle (z_1 and a) are large compared to the corresponding values for the ions of opposite sign is

$$p = n_1 kTz_1/z_2 - e^2 n_1 z_1^2 \sigma/6\, D\lambda, \quad (24)$$

where σ is given by

$$\sigma = 3\beta^{-3}[1+\beta-(1+\beta)^{-1}-2\ln(1+\beta)], \quad (25)$$

$$\beta = a/\lambda \quad (26)$$

and a is the effective distance of nearest approach of the negative and positive particles or ions. In the present case a is approximately the *radius* of the micelle

Equation (24) can be brought to a simpler form by substituting

$$B = e^2 z_1 z_2/2DkT = 3.50\times 10^{-8} z_1 z_2 \text{ cm}, \quad (27)$$

if we take $D = 81$, $T = 293°\text{K}$. Here B is the "Bjerrum[35] radius", within which the potential energy (to remove an ion to ∞) exceeds $2kT$. We thus obtain

$$p = n_1 kT(z_1/z_2)(1-B\sigma/3\lambda). \quad (28)$$

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[34] P. Deybe and E. Hückel, *Physik. Zeits.* **24**, 185 (1923). See especially Eqs. (37) and (33).

[35] N. Bjerrum, *Trans. Faraday Soc.* **23**, 433 (1927).

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By differentiating with respect to λ, taking p, n_1, and σ as dependent variables, by making use of Eqs. (25), (26), (14), and by putting $dp/d\lambda = 0$, we find, without making further approximations, that p becomes a maximum when the following condition is fulfilled:

$$a/\lambda+\lambda/a+2 = B/2a. \tag{29}$$

TABLE III

Conditions under which p is a Maximum. By Eqs. (32), (29), (25), (28) *and* (34)

a/λ	$wz_1/\varrho z_2$	B/a	σ	$1-B\sigma/3\lambda$	$\eta_1 z_2$
0.4	0.0027	9.8	0.598	0.220	14.0
0.6	0.0071	8.53	0.486	0.169	10.7
0.8	0.0132	8.10	0.403	0.130	9.0
1.0	0.021	8.00	0.341	0.068	8.0
1.2	0.030	8.07	0.293	0.056	7.4
1.4	0.040	8.23	0.254	0.0242	6.8
1.6	0.051	8.45	0.223	−0.005	6.5

The value of a/λ can be expressed in terms of B/a by combining Eqs. (14) and (27):

$$(a/\lambda)^2 = 8\pi a^3 n_1 (B/a)(z_1/z_2). \tag{30}$$

If ϱ is the density of the micelles and w the concentration of the sol in grams per ml, then

$$w = (4\pi/3)a^3 n_1 \varrho \tag{31}$$

and therefore in place of Eq. (30) we have

$$(a/\lambda)^2 = 6(wz_1/\varrho z_2)B/a. \tag{32}$$

The potential V_1 at the surface of the micelle of radius a according to Debye and Hückel is

$$V_1 = ez_1/Da(1+a/\lambda). \tag{33}$$

Combining this with Eqs. (10) and (27)

$$\eta_1 = 2B/az_2(1+a/\lambda). \tag{34}$$

In order that p shall have a maximum value as n_1 increases Eq. (29) must be satisfied. The minimum value that B/a can have is 8 and this is reached when $a = \lambda$. Column 3 in Table III gives B/a for other values of a/λ. The 5th column shows that the coefficient of $n_1 kT$ in Eq. (28) becomes negative for $a/\lambda > 1.6$, indicating that the Debye-Hückel equation is not applicable to such high concentrations which make λ small compared to the radius of the micelle. The Debye-Hückel theory, although it is frequently used under such conditions, cannot be expected to be valid for large values of $\eta_1 z_2$ for in its derivation $\epsilon^{\eta z}$ was replaced by $1+\eta z$.

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At low values of a/λ, $\eta_1 z_2$ increases to very high values. The conditions for the validity of the theory are most nearly fulfilled for values of a/λ from 1.0 to 1.4. Here the value of B/a is approximately 8, and thus by Eq. (27) the charge on the micelles needed to give a maximum value of p is roughly $z_1 = 2\times 10^8 a/z_2$.

With these large charges, considerably larger than we calculated in Table II, the concentrations needed for coacervation by column 2 are very much lower than found in Table II and are lower than given by experiment.

Potential Distribution Near Plane Surfaces

In connection with previous studies of metallic surfaces in caesium vapor at high temperature, the following equation was derived[28] for the potential distribution:

$$\theta = -ln \tanh (\eta/4), \tag{35}$$

where

$$\theta = x/\lambda, \tag{36}$$

x being the distance from the plane surface and λ the Debye distance given by Eq. (14).

Equation (35) is a special solution of the fundamental equation

$$2\frac{d^2\eta}{d\theta^2} = \epsilon^{\eta} - \epsilon^{-\eta} \tag{37}$$

for the case that the potential gradient vanishes at $x = \infty$.

A plot of Eq. (35) is shown in Fig. 3 by the curve *ABCD*. For low values of η Eq. (35) approaches the limiting form

$$\eta = 4\epsilon^{-\theta}, \tag{38}$$

whereas for high values of η the limiting curve is

$$\theta = 2\epsilon^{-\eta/2}. \tag{39}$$

These two curves are given in Fig. 3 by *FCD* and *ABE*.

The curve *FCD*, as given by Eq. (38), corresponds to the Debye-Hückel theory. Thus we can replace the actual potential V_1 of a large colloid particle, having approximately a plane surface ($a \gg \lambda$), by the corresponding potential calculated from the curve *FCD*, and, for values of η less than about 1.5, obtain the same potential distribution as if we used the Debye-Hückel theory.

The portion of the curve *AB* rises to infinity at $\theta = 0$. Thus apart from a very small displacement $\Delta\theta$ the potential distribution near a charged surface is independent of the charge, provided the potential corresponds to values $\eta > 5$.

From this theory it follows that the potential distribution around large particles, at distances greater than about 0.8λ, can be calculated by the

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ordinary Debye-Hückel theory if one replaces the true value of η_1 by the fictitious value $\eta_f = 4$. For large spherical particles with $\eta_1 > 5 (V_1 > 0.125$ volt) we may put $\theta = (r-a)/\lambda$ and obtain from Eq. (38)

$$V = 4kT/e \exp[-(r-a)/\lambda]. \tag{40}$$

The potential distribution about a point charge according to the approximate Debye-Hückel theory is

$$V = (ez_1/Dr) \exp(-r/\lambda). \tag{41}$$

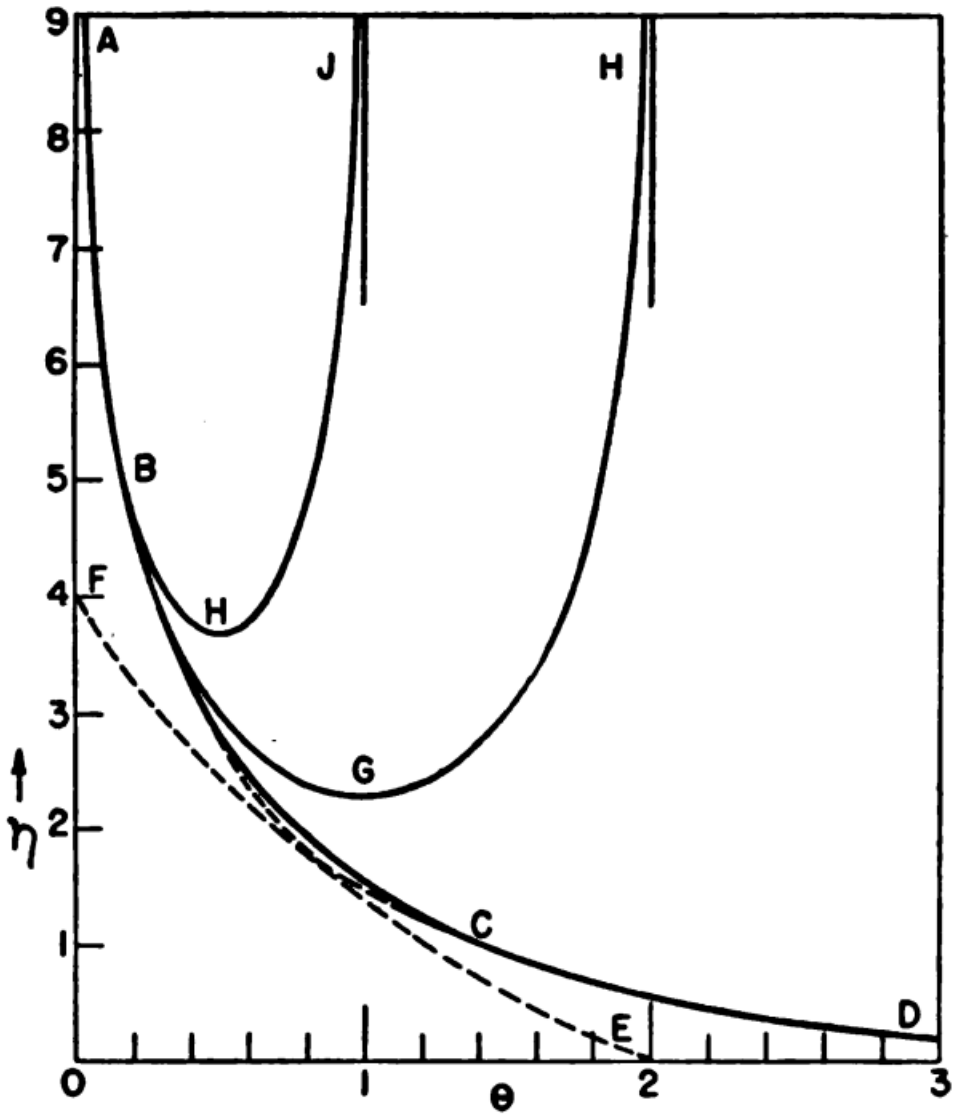

FIG. 3. Potential distributions between parallel plates in an electrolyte.

Since $r \geqslant \lambda$ we can replace r in the coefficient of the exponential factor by a and then by eliminating V between (40) and (41) we find

$$z_1 = (4DkTa/e^2) \exp(a/\lambda) = 0.57 \times 10^{-8} a \exp(a/\lambda). \tag{42}$$

Thus, if we take a point charge $z_1 e$ as given by Eq. (42) and apply the simple potential distribution law of Eq. (41) we will obtain the same distribution as is given by Eq. (40) for all values of r greater than a. The charge z_1, however, will have to be greater than that needed if we were dealing with an ion of radius a.

We are now in a position to make a comparison between the two forms of the Debye-Hückel theory which we have used corresponding to Tables II and III or to the first and second approximations which we shall refer to as A and B. Let us assume that z_1 in each case is so chosen that the potential distributions are the same for $r > a$. The essential difference between the two theories is that they give entirely different distributions for values of $r < a$.

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Thus in Case A within the sphere of radius a there will be a distribution of ions of the opposite sign to that of the micelle, so that this is a kind of storage space for ions. As the concentration increases, the number of ions that are drawn into this space increases. The effect of this withdrawal of ions from solution is to decrease the pressure p from the value given by Eq. (7).

In the Case B the effect of taking a finite radius a is to exclude ions from the interior of the sphere so that the storage space is absent. Therefore, as the concentration increases, fewer ions are bound by the charges on the particles than in Case A. We see, therefore, the physical reason for the marked difference between the calculated data of Table III and the theoretical and experimental data of Table II.

The problem before us is to consider the mechanism of unipolar coacervation. This phenomenon will naturally occur best in colloids whose particles are highly charged, so that we may take $\eta_1 > 5$. We see from Fig. 3 that close to the surface of the particle where $\theta < 1$ the potential rises faster than the Debye-Hückel curve *FCD*. Thus close to the surface of the micelle there will actually be a higher concentration than was given by the theory B. This excess of bound ions close to the surface produces an effect equivalent to that of the storage space in Case A.

For this reason, Theory A, which assumes a point charge, for high values of η_1 will presumably give a better approximation than Theory B. A closer comparison of the data of Tables II and III suggests that Theory A gives too great a storage space, while Theory B gives none. It would seem, therefore, as though a further development, which we may call Theory C, would be desirable in which we take, instead of a point charge, at the center, a sphere of radius a_2 where $a_2 < a$. Then the charge z_1 on this smaller sphere can be chosen to make the storage space between the two spheres approximately equivalent to that which is due to the difference between the two curves *ABCD* and *FCD* in Fig. 3.

In Theory C we can still use Table III by replacing a by a_2. If we take $a_2 = a/8$ we would make $B/a = 1$ and would bring η to values where the Debye-Hückel theory would be applicable.

In this way, by choosing a suitable value for a_2/a, we can cover transitions between Theories A and B. Of course, closer examination might show that in place of Eq. (25) we would have some other relation to give σ in terms of a/λ. It is also possible that the ratio a_2/a should be a function of the concentration. It hardly seems worth while to develop a theory along such lines until we have far better quantitative experimental data on unipolar coacervation with colloids having particles of known character.

For the present we may conclude that neither of the two forms A or B of the Debye-Hückel theory that has been proposed is applicable quantitatively to the problem of coacervation. The A theory fits available data far better

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than the B theory, and there are good theoretical reasons why this should be true. Moreover, it is clear that the attractive forces given by the Debye-Hückel theory are of the right order of magnitude to account for unipolar coacervation. The lack of quantitative agreement gives no reason to assume that unipolar coacervation involves other than Coulomb forces.

From the foregoing attempts to apply the Debye-Hückel theory to unipolar coacervation it appears that the separation into two phases occurs under conditions where a/λ and B/a are each approximately equal to unity. Under these conditions the charge z_1 which must be assumed to exist on a fictitious micelle having a radius $a_2 = 0.2a$ is of the order of 1 unit for each A unit in the diameter $2a$.

Some of these conclusions are closely related to those of a recent paper by Fuoss[36] where he finds critical transitions in the distribution of ions when $a/\lambda = 0.72$ and where $B/a = 2$. We may conclude that if coacervation occurs it generally occurs under about these conditions. If, however, it fails to occur with rising concentrations, this will probably be in general because of factors such as repulsive forces of the type given by Eq. (12) or forces dependent upon the hydration of the ions.

Repulsion Between Parallel Planes

Equation (35) is the solution of the differential Eq. (37) for the case where $d\eta/d\theta = 0$ at $\theta = \infty$. Let us now consider the problem of two positively charged parallel planes at distance b apart. A complete solution of Eq. (37) can be had in terms of elliptic functions. For our present purposes, however, we are interested in the case where $\eta \gg 1$, so that we can neglect $\varepsilon^{-\eta}$ in Eq. (37). The general solution then becomes

$$\theta = 2 \exp(-\eta_M/2) \tan^{-1} [\exp(\eta - \eta_M) - 1]^{1/2}, \tag{43}$$

where θ is now measured from the median plane at which η has a minimum value η_M.

If we place $\eta = \infty$ we obtain the value of θ at one of the planes.

$$\theta_1 = b/2\lambda = \pi \exp(-\eta_M/2). \tag{44}$$

Now, the planes have forces acting upon them due to the pressure of the ions and to the electric field. The sum of these two forces must, however, be constant across the space between the planes.

The potential distributions between the planes for the two cases where $b = 2\lambda$ and $b = \lambda$ are given in Fig. 3 by the curves $ABGH$ and $ABHJ$ respectively. At the median plane where $\theta = 0$, $d\eta/d\theta = 0$ and there is no electric field. If, then, we get the pressure of the ions at this median plane, we obtain

[36] R. M. Fuoss, *J. Am. Chem. Soc.* **57**, 2604 (1935).

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the total forces acting upon the plates. According to Eq. (9), we then have for the concentration n_M at the midpoint

$$n_M = n_0 \exp \eta_M. \tag{45}$$

The pressure $p = n_M kT$ is then given by

$$p = (2\pi\lambda/b)^2 n_0 kT, \tag{46}$$

but according to Eq. (14)

$$\lambda = [DkT/8\pi e^2 n_0]^{1/2} = 3.07\times 10^{-8} c^{-1/2} \text{ cm}, \tag{47}$$

if $D = 81$, $T = 293$ and c is the molar concentration. By eliminating λ between these equations we obtain

$$p = (\pi/2)D(kT/eb)^2 = 8.90\times 10^{-7}/b^2 \text{ dynes/cm}^{-2}. \tag{48}$$

There is thus a repulsive force which is proportional to the surface area and varies inversely as the square of the distance b between the surfaces. This pressure is independent of the charge on the plates and of the ionic concentration provided the potential V_1 is great enough to make $\eta_1 \gg \eta_M \gg 1$ and the concentration is low enough to make $\lambda > b/3$. These restrictions on the general validity of Eq. (48) result from the neglect of the last term, $e^{-\eta}$, in Eq. (37), and the assumption $\eta_1 = \infty$ in the derivation of Eq. (44).

If we put

$$K = \exp(-\eta_M) \tag{49}$$

and replace η by a new variable φ defined by

$$\sin\varphi = \exp[(-\eta-\eta_M)/2], \tag{50}$$

integration of Eq. (37), without simplifying assumptions, gives

$$\theta = 2K^{1/2}[F(\pi/2, K) - F(\varphi, K)], \tag{51}$$

where $F(\varphi, K)$ is the elliptic integral of the first kind for which tables are available.

The exact expression for the pressure is

$$p = 2n_0 kT \cosh \eta_M = (\pi/2)D(kT/eb)^2 R, \tag{52}$$

where

$$R = 2(\theta/\pi)^2 \cosh \eta_M. \tag{53}$$

When $R = 1$, Eq. (52) reduces to Eq. (48).

The variation of pressure with the distance between the plates is illustrated in Fig. 4 which has been constructed by means of Eq. (51). The ordinates, on a logarithmic scale, measure $\cosh \eta_M$, which, according to Eq. (52), varies in proportion to the pressure acting between the plates. The abscissas, also on a logarithmic scale, give θ_1, which, by Eq. (44), measures the distance b between the plates. The straight line AB corresponds to the inverse square law of Eq. (48).

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The deviations from this limiting expression are of two kinds. When $\theta > 1.5$, or $b > 3\lambda$, the pressure may rise above the values given by Eq. (48); viz., R may exceed unity. These deviations, however, are only 17 per cent at $b = 4\lambda$. At still greater values of b the pressure rapidly approaches the limit $2n_0kT$.

The second factor, the approach of η_M to its limiting value η_1, causes the curves in Fig. 4 to break away from the straight line AB at low values

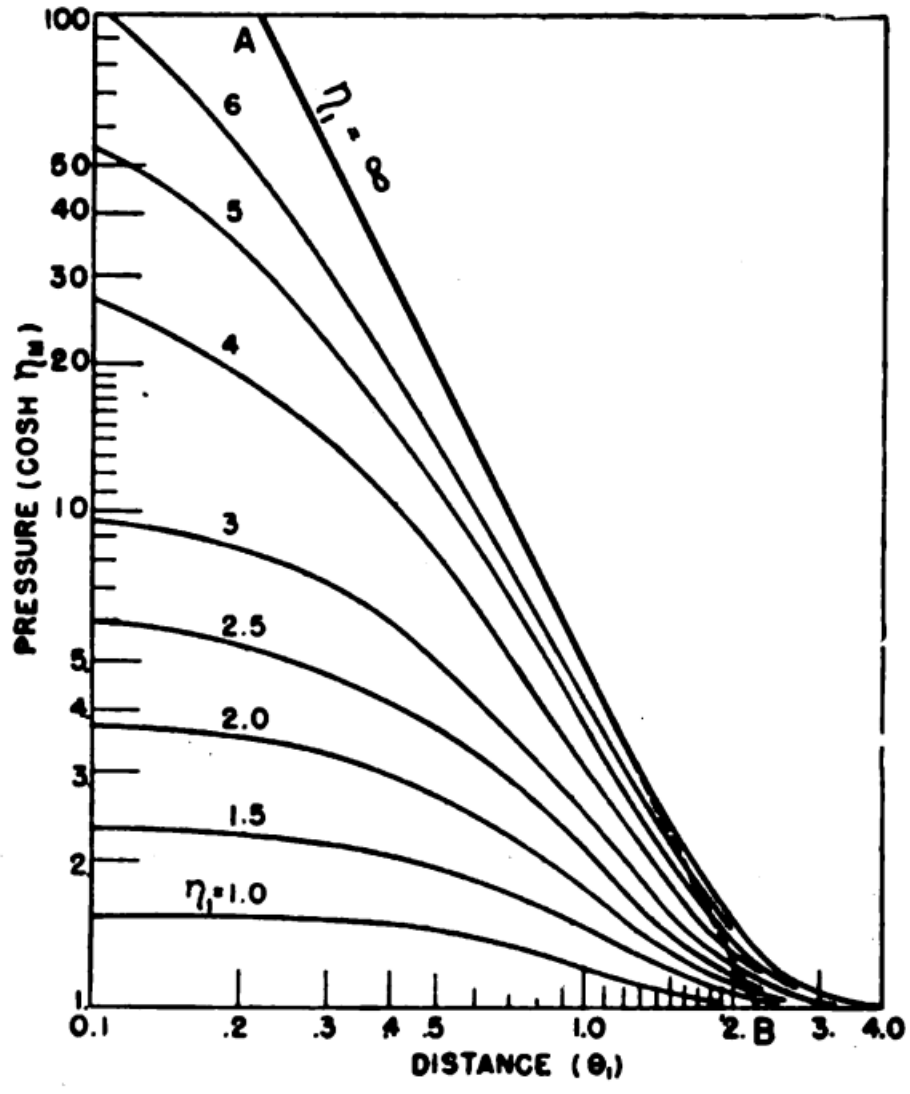

FIG. 4. Double logarithmic plot of the pressure between two plates as a function of the distance between them, for given values of the potentials V_1 on the plates. The actual values of p can be obtained from these data by Eqs. (52), (44), (47) and (10).

of θ_1 and to become approximately horizontal. When $\eta_M > 2$ (or cosh $\eta_M > 3.8$) a good approximation may be had by using Eq. (43) without assuming that $\eta_1 \gg 1$. Substitution of K and φ, as defined by Eqs. (49) and (50), into Eq. (43) gives

$$\theta = 2K^{1/2}(\pi/2-\varphi). \tag{54}$$

The shape of the curves for small values of θ_1, where η_M approaches its limit η_1, may be had by assuming that $\eta_1-\eta_M \ll 1$ in Eq. (50). Eq. (54) then becomes

$$\theta_1^2 = 4(\eta_1-\eta_M)\exp(-\eta_M). \tag{55}$$

The limit of p at low θ_1, shown by Eq. (55) and by the curves of Fig. 4, corresponds to the pressure p_1 given by Eq. (12).

The whole of the pressure calculated from Eq. (52) cannot be regarded as a true repulsive force between the plates. Consider, for example, two colloid

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particles in the form of plates of widths large compared to λ. If these, with their faces parallel, are brought within a distance 3λ there is a pressure between them given by Eq. (52), but on the outer surfaces of each particle there is a pressure $2n_0kT$ acting in the opposite direction. The net repulsive force between the particles thus corresponds to a pressure p_r given by

$$p_r = 2n_0kT(\cosh \eta_M - 1). \tag{56}$$

It has been shown in a recent note[37] that these equations can also be used to calculate the pressure exerted by a solid surface upon the air-water interface of a film of water on this surface. This accounts apparently quantitatively for the Jones-Ray effect according to which very low concentrations of salts lower the capillary rise in surface tension measurements.

Repulsive Forces Between Micelles in Colloids

These equations for the forces between parallel planes are directly applicable to theories of the structure of laminar coacervates such as those formed in iron oxide and tungstic oxide sols that show Schiller layers.

The force given Eq. (48) is of the right magnitude to account for the formation of these coacervates. Thus if $b = 5000$A, we calculate $p = 350$ dynes /cm which is a reasonable osmotic pressure for colloids of this kind. For example if we assume $z_2 = 1$, $z_1 = 1000$ and $p = 350$, Eq. (7) gives $n_1 = 10^{13}$ per cm^3 (roughly 10^{-8} molar). A sol containing 5 per cent by weight of plate-shaped particles 2000A square, of a thickness 250A and density 5 (molecular weight 3×10^8) gives this value of n_1.

The theory of repulsive forces which has been developed in the foregoing pages has been limited to the one-dimensional case to avoid the serious mathematical difficulties involved in the analogous 2- and 3-dimensional problems. The results obtained indicate that forces of the same general nature are effective in all types of unipolar coacervation, whether they involve 1-, 2- or 3-dimensional structures. There are, however, some differences that should be pointed out.

Three types of coacervates may be recognized which differ in the lattice, arrangement of their particles:

One-dimensional coacervation. Iron oxide and tungstic oxide coacervates (Schiller layers) have plate-shaped particles arranged in parallel planes (1-dimensional lattice) with no regularity of distribution within the plane.

Two-dimensional coacervation. The tobacco virus coacervates and V_2O_5 tactoids are examples in which the rod-shaped micelles are arranged in a 2-dimensional lattice without regularity in an axial direction.

Three-dimensional coacervation. The white bentonite sols, although they contain plate-like micelles, from coacervates whose particles are arranged in

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[37] I. Langmuir, *Science* **88**, Nov. 5 (1938).

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a 3-dimensional lattice. There are probably numerous other cases where particles are in 3-dimensional amorphous arrangements (isotropic liquids).

In each case the dilute phase in equilibrium with the coacervate has a 3-dimensional amorphous arrangement of its micelles. This fact seems to be essential for the coexistence of the two phases. To make this clear let us consider the possibility of coacervation in a 1-dimensional system such as that represented in Fig. 4. A plot of p against $1/\theta$ should give a kind of "equation of state" that can be compared to Fig. 2. According to the theory we have given we see, however, that for the 1-dimensional system (Fig. 4), there can be no maximum value of p at large values of θ_1 (low concentrations) and therefore a separation into two phases cannot occur.

The actual existence of 1-dimensional coacervates therefore depends upon the 3-dimensional character of the dilute phase. This means that certain dilute 3-dimensional sols must have higher osmotic pressures p than more concentrated 1-dimensional coacervates.

This difference between the 1- and 3-dimensional phases appears to depend upon the fact that ion association in a 3-dimensional electrolyte becomes negligible at infinite dilution but this does not occur in a 1-dimensional system. Thus in the phase having the 3-dimensional structure the pressure by Eq. (7) is large because z_1 is large, but in the phase having the 1-dimensional structure the effective charge z_1 may be smaller because many of the ions are bound more firmly by the particles (greater ion association).

A complete theory of even 1-dimensional coacervation must therefore involve a calculation of the pressure in a phase having a 3-dimensional arrangement of micelles.

The Potential V_1 and the ζ-Potential

It is known[29] that the ζ-potential, which is calculated, from the electric mobilities of particles, is generally much less than the thermodynamic or electrochemical potential. What value should be used for V_1 in the equations that have been derived?

It is of interest that practically all the values of ζ given in Abramson's book[29] lie below a rather definite limit of 100 mv. This corresponds to $\eta = 4$, which is the value at the point F in Fig. 3 where a very rapid rise in η begins.

By differentiation of Eq. (39) we find that the potential gradient at the surface of a large particle is given by

$$\begin{aligned} dV/dx &= -(kT/e\lambda) \exp(\eta_1/2) \\ &= -(0.025/\lambda) \exp(\eta_1/2) \text{ volts/cm.} \end{aligned} \tag{57}$$

With a $10^{-5}\,M$ salt solution, $\lambda = 10^{-5}$ cm and the potential gradient corresponding to $\eta_1 = 4$ is then 19,000 volts/cm.

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In a discussion of the dielectric constants of dilute salt solutions Debye[38] has calculated that strong electric fields near the ions cause a dielectric saturation. The effect is the same as if the water in regions of field strength exceeding 150,000 volts/cm contributed nothing to the dielectric constant. Actually, of course, the loss of dielectric power is gradual and Debye gives a curve showing the calculated values of D as a function of the distance from the center of the ion.

It is perhaps possible that fields of the order of 20,000 volts/cm which exist when $\eta_1 > 4$ cause an interference in the motions of ions which accounts for the limitation in the observed values of ζ. Probably far higher potential gradients, of the order of 150,000 volts/cm (corresponding to $\eta_1 = 8$), are needed to give a layer of water of hydration (impenetrable to ions).

It seems therefore that when ζ is small, V_1 and ζ are equal, but when ζ approaches its limit of about 100 mv, V_1 can rise considerably above 100 mv. Contact potential measurements of monolayers of proteins and fatty acid derivatives on water give potentials as high as 400 mv. It seems that similar or even higher potentials must be active in many colloids.

Bipolar Coacervation

The cases of coacervation most intensively studied by Bungenberg de Jong have been those in which there are colloidal particles of both signs. With these bipolar coacervates, if V_1 is to remain unchanged for particles of both kinds, the electric fields and the charges on the micelles increase when the concentration increases, whereas with unipolar coacervates the fields decrease. The fact that the particles in the bipolar coacervates remain separated by considerable distances and do not come into contact proves the presence of some other kind of repulsive force than that given by Eq. (48). Hydration seems to be the most reasonable explanation.

The very intense fields that develop when the particles come close together are apparently able to draw water in between the particles and so hold them apart.

It seems, therefore, that Bungenberg de Jong's working hypothesis for this type of coacervation should be accepted. It should be noted that in bipolar coacervates the particles are far closer together than they are in such unipolar coacervates as bentonite, tobacco virus and iron oxide sols.

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[38] P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929), p. 118.

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REGIONS OF REVERSED MAGNETIZATION IN STRAINED WIRES

With K. J. SIXTUS as co-author

Physical Review
Vol. XXXVIII, No. 11, 2072, December (1931).

IN A PAPER on the propagation of large Barkhausen discontinuities along wires[1], it has been shown that under certain conditions a phase boundary could be made to move along a wire. The two phases separated by the boundary were distinguished by the direction of magnetization which was axial but of opposite sign. In order to obtain propagation, the main field H, to which the wire was subjected, had to exceed a critical value H_0.

By a small "stopping coil" a local field H_s can be produced opposing H and reducing the field in a short portion of the wire below H_0. Two search coils are placed on opposite sides of the stop coil and the change in induction in these places is measured ballistically. When the propagation is started from one end, the coils show to what extent the wire has changed from phase I to phase II. If the stopping field is below a critical value, complete reversal is indicated in both coils. If, on the other hand, H_s exceeds this critical value, a change is only observed in the first search coil, no change occurring in the second coil on the other side of the stop coil. This shows that the discontinuity has been stopped and by repeating the experiment with search coil I in different places along the wire, the part of the wire has changed from phase I to phase II can be found.

The "frozen" discontinuity, like the moving one, is cone-shaped, but its length (of the order of 10 cm) is smaller and depends on H. If now a second stopping field is applied in a place along the boundary region, and the first stopping field is removed, the tail of the boundary is held by the second coil. The front edge, however, no longer held by the first stop coil, acts as a nucleus to start propagation over the rest of the wire. The shape of the phase boundary can be determined ballistically as before and is that of a long and narrow kernel, symmetrical with respect to its center. (See Fig. 1.) The same result can be obtained by starting the propagation from both ends of the wire with one stop coil in its center. An analysis of the resulting magnetic field in the boundary region agrees with the hypothesis that the field at the boundary must be H_0.

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[1] K. J. Sixtus and L. Tonks, *Phys. Rev.* **37**, 930 (1931).

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Whereas in the former experiments the propagation was initiated either by artificial nuclei or, in the case of a spontaneous start, by accidental nuclei, whose shape in either case was unknown, we now have produced a nucleus whose size may be varied and whose shape is known, and whose behavior under

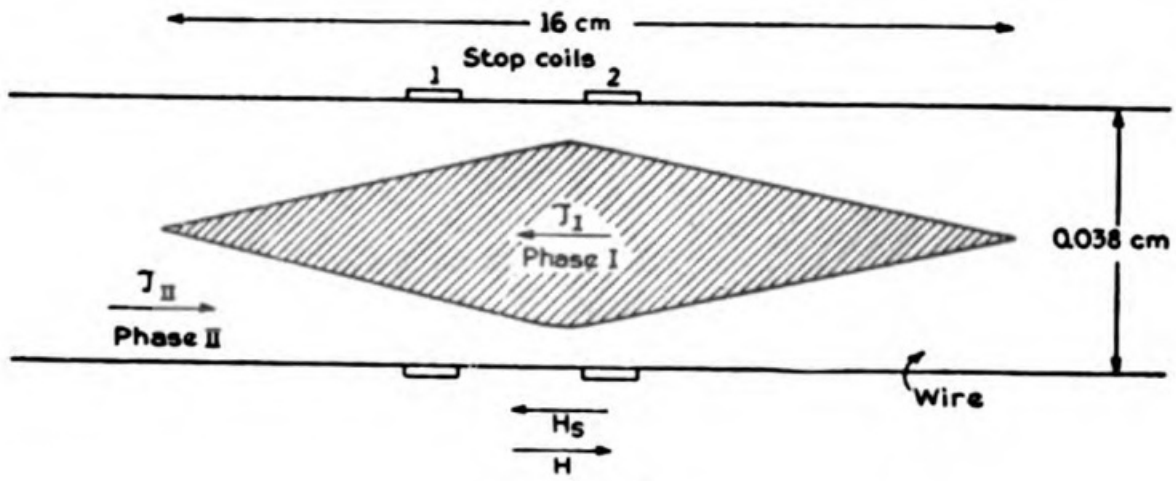

FIG. 1.

various conditions can be studied. The difference and sum of the two values of external field, H_1 and H_2, e.g., at which a certain point of the boundary will start to move in opposite directions, presumably give a direct measure of $2H_0$ and the field due to the internal phase respectively.

A detailed report of these investigations will be published soon.

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APPENDIX I

IRVING LANGMUIR — CURRICULUM VITAE

Born

January 31, 1881

Parents

Charles and Sadie Comings Langmuir

Attended

Public Schools, Brooklyn	1887—1892
Boarding School, Suburban Paris	1892—1895
Chestnut Hill Academy, Philadelphia	1895—1896.

Graduated

Manual Training High School, Pratt Institute	1898

Received degree

Metallurgical Engineer, Columbia University	1903
Doctor of Philosophy, University of Göttingen	1906

Taught

Stevens Institute of Technology	1906—1909

Married

Marian Mersereau	1912

Children

Son, Kenneth
Daughter, Mrs. H. R. Summerhayes

Research Scientist

General Electric Research Laboratory	1909—1950
Associate Director	1929—1950
Consultant	1950—1957

Honorary Degrees Awarded

D.Sc. Northwestern University	1921
LL.D. Edinburgh University	1921
D.Sc. Union University	1923
D.Sc. Columbia University	1925
D.Sc. Kenyon College	1927
D.Sc. Princeton University	1929
D.Ing. Tech. Hochschule, Berlin	1929
D.Sc. Lehigh University	1934

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	LL.D. Union University	1934
	LL.D. Johns Hopkins University	1936
	D.Sc. Harvard University	1938
	D.Sc. Oxford University	1938
	D.Sc. Rutgers University	1941
	D.Sc. Queen's College (Canada)	1941
	LL.D. University of California	1946

Medals Awarded

Nichols Medal	American Chemical Society	1915
Hughes Medal	Royal Society of London	1918
Rumford Medal	American Association for the Advancement of Science	1920
Nichols Medal	American Chemical Society	1920
Stanislao Cannizzaro Award	Royal National Academy of Linnaeus (Rome)	1925
Perkins Medal	Society Chemical Industry (American Section)	1928
Chandler Medal	Columbia University	1929
Willard Gibbs Medal	American Chemical Society	1930
NOBEL PRIZE	Swedish Academy	1932
Popular Science	Popular Science Monthly	1933
Franklin Medal	Franklin Institute	1934
Holley Medal	American Society of Mechanical Engineers	1934
John Scott Medal	Philadelphia Board of Directors of City Trusts	1937
Faraday Medal	Chemical Society (London)	1938
Egleston Medal	Columbia University Engineering Schools Alumni Association	1939
Modern Pioneer of Industry	National Association of Manufacturers	1940
Silver Beaver	Boy Scouts of America	1942
Faraday Medal	Institution of Electrical Engineers	1943
Medal of Merit	United States Army and Navy	1948
Mascart Medal	Academy des Sciences, Societé Française des Electriciens	1948
John J. Carty Medal	National Academy of Sciences	1949
Silver Buffalo	Boy Scouts of America	1950

Died

August 16, 1957

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APPENDIX II

COMPLETE LIST OF PAPERS OF DR. IRVING LANGMUIR AS THEY APPEAR IN THE LANGMUIR MEMORIAL VOLUMES*

VOLUME 1

Low-Pressure Phenomena

Mechanism of Chemical Reactions

1. The Partial Recombination of Dissociated Gases During Cooling. Inaugural dissertation for Doctor's Degree, Göttingen. (1906).
2. The Dissociation of Water Vapor and Carbon Dioxide at High Temperatures. JACS, **28**, 1357 (1906).
3. The Velocity of Reactions in Gases Moving Through Heated Vessels and the Effect of Convection and Diffusion. JACS, **30**, 1742 (1908).
8. A Chemically Active Modification of Hydrogen. JACS, **34**, 1310 (1912).
7. The Dissociation of Hydrogen into Atoms. JACS, **34**, 860 (1912).
18. Note on the Heat of Formation of Hydrogen from Hydrogen Atoms. Phil. Mag., **27**, 188 (1914).
22. The Dissociation of Hydrogen into Atoms. (With G. M. J. Mackay). JACS, **36**, 1708 (1914).
25. The Dissociation of Hydrogen into Atoms. II. Calculation of the Degree of Dissociation and the Heat of Formation. JACS, **37**, 417 (1915); Zeit. f. Electrochemie, **23**, 217 (1917).
37. Dissociation of Hydrogen into Atoms. III. JACS, **38**, 1145 (1916).
9. Chemical Reactions at Very Low Pressures. I. The Clean-up of Oxygen in a Tungsten Lamp. JACS, **35**, 105 (1913).
13. Chemical Reactions at Very Low Pressures. II. The Chemical Clean-up of Nitrogen in a Tungsten Lamp. JACS, **35**, 931 (1913).
27. Chemical Reactions at Low Pressures. JACS, **37**, 1139 (1915).
52. Chemical Reactions at Low Pressures. IV. The Clean-up of Nitrogen by a Heated Molybdenum Filament. JACS, **41**, 167 (1919).
66. Radiation as a Factor in Chemical Action. JACS, **42**, 2190 (1920).

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* Editor's Note: The numbers represent the order in which the papers were published.

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72. Chemical Reaction on Surfaces. G. E. Rev., **25**, 445 (1922); Trans. Faraday Soc., **17**, 607 (1921).
73. The Mechanism of the Catalytic Action of Platinum in the Reactions $2CO + O_2 = 2CO_2$ and $2H_2 + O_2 = 2HO$. Trans. Faraday Soc., **17**, 621 (1921).

VOLUME 2

Heat Transfer — Incandescent Tungsten

Part 1 — *Transfer of Heat*

4. Thermal Conduction and Convection in Gases at Extremely High Temperatures. Trans, Amer. Electrochem. Soc., **20**, 225 (1911).
5. Convection and Conduction of Heat in Gases. Phys. Rev., **34**, 401 (1912).
6. Convection and Conduction of Heat in Gases. Proc. AIEE, **31**, 1011 (1912).
10. Laws of Heat Transmission in Electrical Machinery. Proc. AIEE, **32**, 391 (1913).
11. Convection and Radiation of Heat. Trans. Amer. Electrochem. Soc., **23**, 299 (1913).
12. Flow of Heat Through Furnace Walls: the Shape Factor. (With E. Q. Adams and G. S. Meikle). Trans. Amer. Electrochem. Soc., **24**, 53 (1913).
103. Flames of Atomic Hydrogen. Science, **62**, 463 (1925).
104. Flames of Atomic Hydrogen. G. E. Rev., **29**, 153 (1926).
105. Atomic Hydrogen Arc Welding. (With R. A. Weinman). G. E. Rev., **29**, 160 (1926).
110. Flames of Atomic Hydrogen. Ind. and Engrg. Chem., **19**, 667 (1927).

VOLUME 2

Heat Transfer — Incandescent Tungsten

Part 2 — *Incandescent Lamps and Tungsten*

14. Tungsten Lamps of High-efficiency. I. Blackening of Tungsten Lamps and Methods of Preventing it. II. Nitrogen-filled Lamps. (With J. A. Orange). Proc. AIEE, **32**, 1894 (1913); Trans. AIEE, **32**, 1913 (1913); G. E. Rev., **16**, 956 (1913).
20. The Flicker of Incandescent Lamps on Alternating Current Circuits and Stroboscopic Effects. G. E. Rev., **17**, 294 (1914).
26. The Melting Point of Tungsten. Phys. Rev., **6**, 138 (1915).
34. The Characteristics of Tungsten Filaments as Functions of Temperature. Phys. Rev., **7**, 302 (1916).
111. The Characteristics of Tungsten Filaments as Functions of Temperature. (With H. A. Jones). G. E. Rev., **30**, 408; 310; 354 (1927).

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126. Effect of End Losses on the Characteristics of Filaments of Tungsten and other Materials. (With S. MacLane and K. B. Blodgett). Phys. Rev., **35**, 478 (1930).
151. The Design of Tungsten Springs to Hold Tungsten Filaments Taut. (With K. B. Blodgett). Rev. Sci. Instru., **5**, 321 (1934).
156. Radiation and Absorption of Energy by Tungsten Filaments at Low Temperatures. (With J. B. Taylor), Jour. Opt. Soc. Amer., **25**, 321 (1935).
159. The Heat Conductivity of Tungsten and the Cooling Effects of Leads upon Filaments at Low Temperatures. (With J. B. Taylor). Phys. Rev., **50**, 68 (1936).

VOLUME 3

THERMIONIC PHENOMENA

Part 1 — *Thermionics — Vacuum Pumps*

17. The Effect of Space Charge and Residual Gases on Thermionic Currents in High Vacuum. Phys. Rev., **2**, 450 (1913).
28. The Pure Electron Discharge and its Applications in Radio Telegraphy and Telephony. G. E. Rev., **18**, 327 (1915); Trans. AIRE, **3**, 261 (1915).
65. Fundamental Phenomena in Electron Tubes Having Tungsten Cathodes. (Part I and Part II). G. E. Rev., **23**, 503, 589 (1920).
79. Use of High-power Vacuum Tubes. Electrical World, **80**, 881 (1922).
81. The Effect of Space Charge and Initial Velocities on the Potential Distribution and Thermionic Current between Parallel Plane Electrodes. Phys. Rev., **21**, 419 (1923).
85. A New Photo-electric Effect Reflection of Electrons Induced by Light. Science, **58**, 398 (1923).
91. Currents Limited by Space Charge between Coaxial Cylinders. (With K. B. Blodgett). Phys. Rev., **22**, 347 (1923).
93. Currents Limited by Space Charge between Concentric Spheres. (With K. B. Blodgett). Phys. Rev. **23**, 49 (1924).
133. Diffusion of Electrons back to an Emitting Electrode in a Gas. Phys. Rev., **38**, 1656 (1931).
33. A New Vacuum Gage of Extreme Sensitiveness. (Abstract). Phys. Rev., **1**, 337 (1913).
38. A High Vacuum Mercury Vapor Pump of Extreme Speed. Phys. Rev., **8**, 48 (1916).
44. The Condensation Pump: an Improved Form of High Vacuum Pump. G. E. Rev., **19**, 1060 (1916); Jour. Franklin Inst., **182**, 719 (1916).

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VOLUME 3

THERMIONIC PHENOMENA

Part 2 — Electron Emission and Adsorbed Films

36. The Relation Between Contact Potentials and Electrochemical Action. Trans. Amer. Electrochem. Soc., **29**, 125 (1916).
80. Thermionic Effects Caused by Alkali Vapors in Vacuum Tubes. (With K. H. Kingdon). Science, **57**, 58 (1923).
83. Removal of Thorium by Positive Ion Bombardment. (With K. H. Kingdon). Phys. Rev., **22**, 148 (1923).
87. Electron Emission From Caesium-covered Filaments. (With K. H. Kingdon). Phys. Rev., **23**, 112 (1923).
90. The Electron Emission From Thoriated Tungsten Filaments. Phys. Rev., **22**, 357 (1923).
100. Thermionic Effects Caused by Vapors of Alkali Metals. (With K. H. Kingdon). Proc. Roy. Soc., A, **107**, 61 (1925).
109. On the Surface Heat of Charging. (With L. Tonks). Phys. Rev., **29**, 524 (1927).
121. Contact Potential Measurements With Adsorbed Films. (With K. H. Kingdon). Phys. Rev., **34**, 129 (1929).
127. Electrochemical Interactions of Tungsten, Thorium, Caesium, and Oxygen. Ind. and Engrg. Chem., **22**, 390 (1930).
129. Oxygen Films on Tungsten. I. A Study of Stability by Means of Electron Emission in Presence of Cesium Vapor. (With D. S. Villars). JACS, **53**, 486 (1931).
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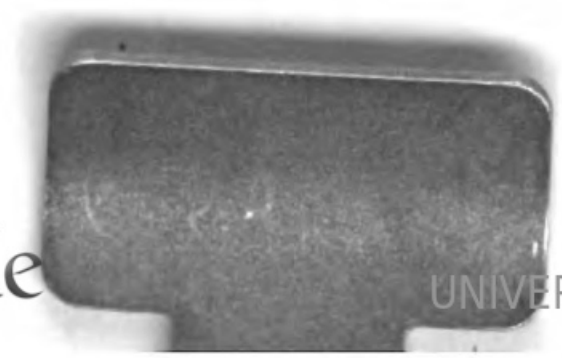

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